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NOTES ON SELENIUM AND TELLURIUM.

BY EDWARD KELLER.

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IN a paper under the above title,[1] published some years ago, I pointed out the difference of behavior of selenium and tellurium, in the dioxide state, towards sulphur dioxide and ferrous sulphate in solutions of hydrochloric acid of various strength. The experiments were conducted under definite conditions, as stated in my original paper, the quantities of the two elements being in every case 0.1 gram each, the quantity of the solution 100 cc., and the acidity varying from 0.5 to 100 per cent., the pure hydrochloric acid meaning the aqueous product of 1.175 sp. gr. Based on quantitative determinations of the two elements precipitated by sulphur dioxide in the cold, and other conditions as already stated, the conclusions reached, were as follows: Selenium is most readily precipitated by sulphur dioxide in strong hydrochloric acid. This precipitation continues to be complete until an acidity of 25 per cent. is reached, the solution being allowed to stand about twenty hours. The precipitation, within that time, becomes nil at an acidity of approximately 3 per cent. The precipitation of tellurium in strong hydrochloric

[1] This Journal, 19, 771.

acid is nil. It begins with an acidity of about 80 per cent. (the time of standing as above), becomes complete at about 60 per cent., and continues to be so until the acidity is reduced to about 10 per cent.

On page 774 of the paper cited is found the following remark: "From the above facts we learn that even with sulphur dioxide in a hydrochloric acid solution of over 80 per cent. acid a separation is possible" (meaning a separation of selenium and tellurium).

A NEW METHOD OF QUANTITATIVE SEPARATION OF SELENIUM AND TELLURIUM.

That selenium is more readily precipitated by sulphur dioxide than tellurium has long been known and the principle has been practically applied, but, it seems, never to quantitative analysis. Since the publication of my paper, above referred to, I have had occasion in numerous instances to determine the two elements in copper analysis, and I have in all cases applied this hydrochloric acid-sulphur dioxide method. When working with a Gooch filter and a suction pump (filter-paper, of course, cannot be used) this separation is a rapid and simple one. My mode of operation is as follows: 100 grams of copper with from 2 to 4 grams of ferrous sulphate, are dissolved in 400 cc. nitric acid (sp. gr. 1.42) and the nitrous fumes expelled. This solution, after diluting and cooling, is made sufficiently ammoniacal to dissolve all the copper. After boiling and settling, the ferric hydroxide containing the selenium and tellurium is gathered on a filter. It must be freed from copper by washing with ammoniacal water, redissolving in acid, and reprecipitation with ammonia (repeatedly if necessary). This ferric hydroxide is then brought into dilute hydrochloric acid solution (not more acid being used than is necessary to dissolve the precipitate), and hydrogen sulphide passed through the cold liquid until saturation. The solution must be cold to retain the selenium sulphide in soluble form in sodium sulphide, and copper must be absent to guard against insoluble cupric selenide. The sulphides are filtered and washed and digested with a solution of sodium sulphide, which latter takes up the sulphides of selenium and tellurium. The solution, after filtering, is acidified with

nitric acid and evaporated to dryness. The latter operation must be performed with care, to avoid loss of selenium dioxide. The residue now contains the dioxides of selenium and tellurium and sodium nitrate, besides some sulphur. To this residue is added 200 cc. of strong hydrochloric acid, and boiled until all the nitro-hydrochloric acid (its presence being due to the nitrate) is destroyed, and the two elements, which may have been oxidized to the selenic and telluric form, are reduced to the selenous and tellurous state. After cooling, the solution is filtered off from the sulphur and the insoluble halide through a Gooch filter, and the residue washed several times with strong hydrochloric acid; the latter, however, need not be of more than 90 per cent. strength. The filtrate is now ready to be saturated with sulphur dioxide gas, conveniently generated by copper borings and concentrated sulphuric acid, which will precipitate the selenium alone under the given conditions. After settling, which may be accelerated by warming, the selenium is gathered on a weighed Gooch filter and washed with hydrochloric acid (90 per cent.) about three times. Here the filtrate is set aside, and the selenium freed of salts, etc., by washing successively with warm, dilute hydrochloric acid, pure water, and strong alcohol. After drying it is weighed. The filtrate containing the tellurium is increased to double its volume with pure water. With the small quantities of tellurium present in copper, the amount of sulphur dioxide held in solution is generally sufficient to precipitate that element completely upon boiling; however, it is safer to boil the dilute solution for some minutes, and while doing so to conduct more sulphur dioxide through it. After cooling and settling, the tellurium is filtered, washed, and weighed in the same manner as the selenium.

The following quantitative determinations, for which commercial accuracy only is claimed, were made in proof of the method, the conditions being that 0.1 gram of selenium and 0.1 gram of tellurium, previously converted into dioxide, were jointly dissolved in 100 cc. of 90 per cent. hydrochloric acid, and the further operations performed as previously described:

DETERMINATION OF SELENIUM AND TELLURIUM BY PRECIPITATION WITH SULPHUR DIOXIDE IN HYDROCHLORIC ACID.

Selenium.		Tellurium.	
Weighed in. Gram.	Found. Gram.	Weighed in. Gram.	Found. Gram.
0.1000	0.0983	0.1000	0.0998
0.1000	0.1000	0.1000	0.0986
0.1000	0.1006	0.1000	0.1010
0.1000	0.0994	0.1000	....
0.1000	0.1002	0.1000	0.0993
0.1000	0.1010	0.1000	0.1013
Av'r'ge 0.1000	0.0999	0.1000	0.1000

The selenium in every case proved to be free of tellurium by its complete solubility in potassium cyanide. Nor could selenium be detected in the filtrates with ferrous sulphate by either increasing or decreasing the strength of the acid. In short, the separation is complete.

In a paper by Mr. Victor Lenher[1] are to be found the following remarks: "When sulphur dioxide is brought into contact with such a strong solution, selenium should be precipitated free from tellurium according to Keller. When sulphur dioxide was introduced into this solution a red precipitate formed, showing selenium just precipitated. It appeared to darken, however, when the liquid was saturated. On boiling, the precipitate agglomerated into a mass which much resembled selenium, but on separating it by means of potassium cyanide it was found to consist of 3.2 grams of selenium and 28.3 grams of tellurium. This seems to indicate that tellurium and selenium cannot be perfectly separated by sulphur dioxide in strong hydrochloric acid solution."

Mr. Lenher worked with 5 pounds of tellurous and selenous material. He does not mention the quantity of acid he used. His conditions were, therefore, probably radically different from those as given in my own experiments.

As I could not doubt my own results of often repeated tests, nor Mr. Lenher's assertions, I inferred that the difference in the conclusions arrived at must be due to the difference in the relative masses of tellurium and acid present in the experiments, and I corroborated this by a few simple tests: The oxides of 0.1 gram of selenium and 5 grams of tellurium were dissolved in

[1] "Preparation of Metallic Tellurium," This Journal, 21, 347.

100 cc. of 90 per cent. hydrochloric acid, and the solution saturated with sulphur dioxide. The precipitate, after standing about twenty hours, contained all of the selenium with 2.1 grams of tellurium. In the subsequent tests the acid of the same strength was increased each time by 50 cc., the quantities of selenium and tellurium remaining constant. The quantity of tellurium decreased in each successive precipitation, and became nil when the quantity of acid reached 450 cc. It follows, therefore, that to obtain a perfect separation of selenium and tellurium in strong hydrochloric acid solution by means of sulphur dioxide, the quantity of acid must be about 100 times that of the tellurium.

Numerous chemists have pointed out the error made in determining tellurium in its metallic state, it being due to slight oxidation. Mr. F. H. D. Crane[1] found this error to be from 0.3–0.6 per cent. over the correct result, when no precautions were taken. Criticism for using this method in industrial practice seems to me entirely unjustified. Although accuracy is always essential, the practical chemist must be able to discriminate between accuracy and pedantry. For example: Our copper rarely contains as much as 0.01 per cent. of tellurium, and we should find, according to Mr. Crane, when using 100 grams of copper, from 0.01003 to 0.01006 instead of 0.01 gram of the element, a difference absolutely beyond detection and of no importance whatsoever in ordinary work. In fact, the chemist would find, in practice, that with more scientific methods ± 3 or 6 per cent. would often be far from covering the differences between his own duplicates, or those of other equally conscientious workers. In substantiation of this I need only refer to the determination of small percentages of precious metals,[2] upon which large commercial interests depend. With silver, which occurs in larger quantity than tellurium, determinations often differ ± 3 to 5 per cent. from the mean. With gold, occurring in smaller quantities, these variations rise as high as ± 25 per cent.

BALTIMORE, March, 1900.

1 "A Contribution to the Knowledge of Tellurium," Dissertation, Johns Hopkins University, 1898.

2 "Assays of Copper and Copper Matte," *Trans. A. I. M. E.*, 25, 250.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, U. S. DEPARTMENT OF AGRICULTURE, NO. 37.]

THE ESTIMATION OF ALUMINA AND FERRIC OXIDE IN NATURAL PHOSPHATES.[1]

BY F. P. VEITCH.

Received March 22, 1900.

THE search for an accurate and rapid method for the determination of alumina and iron oxide in the presence of phosphoric acid has occupied the attention of analysts for years, and many methods have been proposed for this difficult operation. It may be said generally that even those methods that have stood the tests of extended use have not escaped severe criticism; they are only accurate within narrow and rigidly defined limits or they are tedious and time-consuming.

Aside from its interest from the scientific point of view, this subject is of importance in its technical and commercial aspects. The value of raw mineral phosphates, which, in the United States alone, for the year 1893, Wiley estimates at $4,157,070,[2] is determined largely by their content of alumina and iron.

In phosphatic slags the estimation of these oxides is more difficult, though possibly not so important.

SOURCES OF ERROR IN THE OLDER METHODS.

The Glaser alcohol, the acetate with its various modifications, and the caustic alkali, methods as carried out by Lasne, Lichtschlag, and by Gladding, have all been severely criticized and the following sources of error pointed out by various observers:[3]

1. In the Glaser alcohol method, the precipitation of manganese with the iron and aluminum phosphates, and solubility of the phosphates in the wash-water. Probably the manganese can be eliminated by a second precipitation in the presence of a large amount of ammonium chloride. Possibly the presence of a large amount of ammonium sulphate may also effect the accuracy of this method, in those cases where the excess of ammonia is com-

[1] Abstract of Thesis presented to the Faculty of the Graduate School of Columbian University and accepted for the degree of Master of Science, June, 1898. Presented to the American Chemical Society, Boston Meeting, 1898.

[2] U. S. Department of Agriculture, Yearbook, 1894.

[3] Wiley's "Principles and Practice of Agricultural Analysis," Vol. II, pp. 24, *et seq.*

pletely removed by boiling. Aluminum phosphate is noticeably soluble in a strong sulphate solution, which is neutral or faintly acid from SO_3.

2. In the acetate method and its variations, the precipitation of the lime with the iron and aluminum phosphates, solubility of aluminum phosphate in cold acetate solutions, solubility and dissociation of iron and aluminum phosphates in water,[1] also when the phosphates are fused with sodium carbonate, and the iron determined by precipitation with ammonia, the contamination of the iron with calcium phosphate, which is not always entirely decomposed by fusion. Of these the most serious sources of error are the first and the last mentioned.

3. In the caustic alkali methods, there is danger of some of the aluminum being held by the voluminous precipitate produced by the alkali; there is also danger of alumina being precipitated if much carbon dioxide is absorbed; Lasne and Lichtschlag have shown that while the method is long it gives accurate results if properly conducted. Blaltner and Brasseur[2] have recently investigated the more important methods and conclude:

"The acetate method should be discontinued; figures for alumina are nearly always too low."

Glaser method (alcohol) gives accurate results in the absence of manganese.

The caustic soda method, as carried out by Lasne, gives exact results. Gruber's and Gladding's methods are condemned.

In view of these many sources of error in the conventional methods, considerable time has been devoted to the study of a method that, it is hoped, is free from most of the above-mentioned objections. It is an adaptation, so far as possible, of the good points of the present best methods. From the precipitating reagent, it may be designated

THE THIOSULPHATE METHOD.

The use of a soluble thiosulphate for the separation of alumina from iron and aluminum from several other metals seems to be due to G. Chancel.[3] Later it was used by Stead and by Car-

[1] *Chem. Ztg.* (1897), p. 264; also Fresenius.
[2] *Bull. Soc. Chim.* [3], 17, 18, No. 15.
[3] *Compt. rend.*, 46, 98.

not;[1] by the latter for the separation of aluminum as phosphate, in the presence of ammonium acetate, from iron. Lasne[2] also uses it to precipitate aluminum phosphate in the presence of ammonium acetate, after removing iron, lime, etc., with caustic soda.

From the available literature on the subject it seems that a method based on the separation of aluminum phosphate from iron and lime by a thiosulphate and ammonium chloride alone, may be used for the determination of aluminum in the common natural phosphates.

Considerable work has been done with the method to gain familiarity with it and to test its applicability under various conditions and in the presence of various salts. For this work a chemically pure aluminum sulphate was prepared in which alumina has been carefully determined. This salt was used for all the tests.

The preliminary work under varying conditions, following the method as laid down by Chancel and by Carnot, did not always give concordant results, frequently being low. A brief study suggested the cause of this, and the addition of a considerable quantity of ammonium chloride led to much better results. The principle upon which the method is based is the insolubility of aluminum phosphate in a strong neutral solution of ammonium chloride. The thiosulphate has nothing to do with the precipitation, except that it is an exact method of obtaining the desired neutrality. Thomson[3] has devised a method in which he makes use of this principle, neutralizing with ammonia, using a delicate indicator to determine neutrality.

Study of the Proposed Method.—One of the first problems presented in the study of any method for the determination of alumina as phosphate is the composition of the ignited phosphate. Observers do not agree as to this. While all agree that the normal phosphate is only obtained in the presence of an excess of phosphoric acid, they do not agree that it is always obtained, even under these conditions.[4]

[1] Blair's "Chemical Analysis of Iron," second edition, 185, 186.

[2] *Bull. Soc. Chim.*, **15**, 118.

[3] *J. Soc. Chem. Ind.*, **15**, 868.

[4] *Chem. Ztg.* (1897), pp. 264, and **21**, 116; Wiley's "Principles and Practice of Agricultural Analysis," Vol. II, p. 24; Blair's "Chemical Analysis of Iron," second edition, 185; S. C. Agr. Expt. Sta., Bull. No. 2.

Wash Solutions.—It seems that the solution of this problem can only be obtained by a study of the solutions used in washing the precipitate. Besides waters of all temperatures, solutions of various salts, such as 5 per cent. ammonium nitrate, ammonium chloride, 1 per cent. ammonium nitrate plus 0.02 per cent. ammonium phosphate, and dilute ammonium acetate, have been proposed and used by many investigators. These various washes possibly account for the variations from the normal, so frequently noted. In the brief mention of some of the observed sources of error in the conventional methods it was shown, by numerous authorities, that the recently precipitated phosphates of iron and aluminum, when freed from adhering salts, are slightly soluble, or rather are dissociated, in water of any temperature. Those who have apparently used water successfully as a wash probably did not wash enough, only three or four times, to remove the adhering salts. Cold ammonium or sodium acetate also slowly dissolves aluminum phosphate.

The effects of the following wash liquors have been studied:

Water at from 60° to 70° C.

5 per cent. ammonium nitrate at from 60° to 70° C.

1 " " " " " " 60° " 70° C.

5 " " " " and 0.02 per cent. ammonium phosphate at from 60° to 70° C.

Method of Study.—Various quantities of the C. P. aluminum sulphate were placed in a 12-ounce beaker with a solution of 2 grams of ammonium phosphate, the resulting precipitate dissolved in hydrochloric acid, and 25 cc. of a 50 per cent. solution of ammonium chloride added. The solution was then made alkaline with ammonia and the precipitate just dissolved with hydrochloric acid, noting approximately the number of cubic centimeters required after the solution had become acid; the solution was then diluted to about 250 cc., and for each cubic centimeter of hydrochloric acid added to the acid solution 5 cc. of a 50 per cent. solution of ammonium thiosulphate were added dropwise, the beaker covered with a watch-glass, the solution boiled half an hour, filtered, washed, dried, and ignited to constant weight.

The results are given in Table I. All results in the work have been corrected by blank determinations on the reagents

TABLE I.

Wash solution.	Washings. Times.	Volume. cc.	Al_2O_3. Theory. Mgs.	Al_2O_3. Found. Mgs.	Error. Mgs.
Water 60° to 70° C.....	40	500	159.7	155.9	—3.8
" 60° " 70° C.....	20	250	39.9	38.2	—1.7
5 per cent. ammonium nitrate, 60° to 70° C.....	20	250	39.9	39.8	—0.1
5 " " " 60° to 70° C.....	20	250	79.8	79.6	—0.2
5 " " " 60° to 70° C.....	20	250	79.8	80.1	—0.3
5 " " " 60° to 70° C.....	50	650	79.8	78.9	—0.9
5 " " " 60° to 70° C.....	50	650	79.8	79.3	—0.5
1 " " " 60° to 70° C.....	20	250	39.9	39.3	—0.6
1 " " " 60° to 70° C.....	20	250	79.8	79.2	—0.6
1 " " " 60° to 70° C.....	20	250	79.8	78.8	—1.0
1 " " " 60° to 70° C.....	20	250	79.8	77.4	—2.1
1 " " " 60° to 70° C.....	20	250	79.8	79.2	—0.6
1 " " " 60° to 70° C.....	20	250	79.8	79.2	—0.6
5 " $(NH_4)_2NO_3$+0.02 per cent. $(NH_4)_2HPO_4$.	20	250	79.8	80.9	—1.1
5 " " " " " " .	20	250	79.8	80.2	—0.4

employed; and all precipitations were made in the presence of an excess of phosphoric acid.

An examination of the table shows that, of the wash solutions, 5 per cent. ammonium nitrate washing twenty times gives practically theoretical results. As many as 50 washings with this solution give results slightly low but still good. The other solutions were rejected as they showed a decided solvent effect, except the ammonium nitrates plus ammonium phosphate, upon prolonged washing. Twenty washings were required to free the precipitate from chlorides, sulfates, and ammonium phosphate. In all succeeding work 5 per cent. ammonium nitrate was used, washing twenty times unless otherwise stated. Long heating with the blast, ten to twenty minutes, was required to reduce to constant weight.

Composition of the Ignited Aluminum Phosphate.—The phosphoric acid, in the aluminum phosphate washed twenty times with 5 per cent. ammonium nitrate, was carefully determined by precipitation with molybdate solution, washing the precipitate of ammonium phosphomolybdate with dilute nitric acid, and washing the final precipitate free of chlorides.

	Theory. P_2O_5. Mgs.	Found. P_2O_5. Mgs.
a	58.2	58.8
b	...	58.7
c	...	58.8
	Average,	58.8

The salt obtained under the above-mentioned conditions seems to be the normal phosphate, $AlPO_4$.

THE EFFECT OF THE PRESENCE OF SALTS OF SOME OTHER METALS.

Effect of Iron Salts.—Five grams of ammonium ferric alum dissolved in water, 2 grams of ammonium phosphate added, and treated as for aluminum phosphate, washing twenty times with ammonium nitrate, gave:

	Calculated as alumina. Mgs.
a	4.5
b	0.0
c	1.3
d	0.0

Precipitated while slightly warm.

Another series precipitated twice gave:

	Calculated as alumina. Mg.
a	0.4
b	0.0
c	0.0
d	0.0

Solutions containing aluminum sulphate, ammonium phosphate, and 5 grams of ammonium ferric alum precipitated once with ammonium thiosulphate, gave:

	Theory. Mgs.	Al_2O_3 found. Mgs.
a	78.9	86.4
b	23.9	28.2

Both contained iron.

Similar solutions precipitated twice with sodium thiosulphate, gave:

	Theory. Mgs.	Al_2O_3 found. Mgs.
a	39.9	39.4
b	39.9	40.8

These precipitates contained no iron.

Therefore, in the presence of large quantities of ferric iron, two precipitations only are necessary to separate the iron.

Effect of Calcium Salts.—Two grams of calcium phosphate, precipitated once, gave:

a, Nothing.

b, "

Aluminum phosphate plus 2 grams calcium phosphate, precipitated once, gave:

	Theory. Mgs.	Al_2O_3 found. Mgs.
a	79.8	80.1
b	79.8	80.8
c	79.8	81.0
d	23.9	24.3
e	79.8	80.2
f	79.8	79.3

a, *b*, *c*, and *d* were washed twenty times with 5 per cent. ammonium nitrate; *e* and *f* were washed fifty times.

The error produced by the presence of calcium salts alone is

not so great as that produced by iron salts. In this case it seems probable that the error is produced by the well-known property of the aluminum precipitates of carrying down other salts mechanically. Two precipitations separate completely aluminum phosphate from very large quantities of iron and of lime, as is shown by the following data:

$Al_2(SO_4)_3$. Gram.	$Ca_3(PO_4)_2$. Gram.	$NH_4Fe(SO_4)_2$. Gram.	Al_2O_3 Theory. Mgs.	Al_2O_3 Recovered. Mgs.
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	39.9	39.6
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	19.9	18.8
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	19.9	18.8
$\frac{1}{4}$	2	1 iron	39.9	39.7
$\frac{1}{4}$	2	1 "	39.9	39.9

From the foregoing results the conclusion seems warranted that aluminum phosphate can be quantitatively separated by a soluble thiosulphate and ammonium chloride from a hydrochloric acid solution of iron, alumina, and lime phosphates containing only a small amount of sulphates. The statement of many observers, that theoretical results on aluminum phosphates can only be obtained in the presence of an excess of phosphoric acid, has been confirmed by my own work. The error produced by precipitating a second time without adding phosphoric acid amounted in some cases to 2 mgs. alumina.

The Effect of Magnesium, Sodium, and Potassium Salts.—Three solutions containing in 50 cc. the following:

	A. Gram.	B. Gram.	C. Gram.
Calcium phosphate	0.8000	0.7000	.....
Calcium chloride	.....	.....	0.250
Magnesium chloride	0.0200	0.0100	0.0250
Potassium chloride	0.0100	.....	.....
Sodium chloride	.....	0.0100	.....
Iron	0.0185	0.0421	0.0125
Sodium hydrogen phosphate	.....	.....	2.0000
Aluminum sulphate	0.3504	0.1504	0.1000

gave

	A.		B.		C.	
	Theory. Mgs.	Found. Mgs.	Theory. Mgs.	Found. Mgs.	Theory. Mgs.	Found. Mgs.
Alumina	56.0	54.5	24.0	24.2	16.0	15.8
	56.0	56.3	24.0	23.9	16.0	15.8

The above-named salts therefore exert no disturbing influence on the accuracy of the final results.

The Effect of Silica.—It is stated by Carnot[1] that "In the presence of silica the precipitate of aluminum phosphate contains a little silica." I have tried to remove this silica by two precipitations but have failed, the plus error equivalent to Al_2O_3 being,

	Mgs.
a	1.2
b	0.6
c	3.3
d	2.5

In order to secure correct results, therefore, the silica must be removed from the mixture before the separation of the aluminum phosphate.

The Effect of Sulphates.—Removal of silica being a necessary operation it was determined to make the separation by the well-known method based on the insolubility of silica in sulphuric acid. This method, worked out very carefully by Drown,[2] is a very rapid and accurate process, which is used almost exclusively in the determination of silica in pig-iron. Essentially the same method has been worked out and used by others for the determination of silica in furnace products.

While the separation of silica by this method is all that can be desired it was found to be impossible to completely precipitate the aluminum phosphate with a thiosulphate in the filtrate.

From solutions containing various quantities of the sulphates, phosphates, and chlorides of iron, aluminum, and lime, the following results were obtained:

Experiment.	H_2SO_4 present. Grams.			Alumina. Theory. Mgs.	Alumina. Found. Mgs.
2	0.100	1	precipitation	39.9	39.8
11	0.20	1	"	79.8	79.6
12	0.20	1	"	....	80.1
19	0.20	1	"	....	80.1
20	0.20	1	"	....	80.8
20*a*	0.10	1	"	23.9	24.2
33*a*	1.250	2	"	39.9	39.6
34*a*	1.250	2	"	....	40.7

[1] Blair's "Chemical Analysis of Iron," p. 188.
[2] *J. Inst. Min. Eng.*, 7, 346.

Experiment.	H_2SO_4 present. Grams.			Alumina. Theory. Mgs.	Alumina. Found. Mgs.
50	2.800	2	"	....	38.7
35*a*	7.500	2	"	19.9	16.8
36*a*	7.500	2	"	....	18.7
39*c*	7.500	2	"	39.9	37.9
39*d*	7.500	2	"	....	37.8
38*a*	36.000	1	"	31.9	17.2

The presence of more than 1.25 grams of sulphuric acid prevents the complete precipitation of aluminum phosphate, while 2.75 grams give a decided error. The presence of ammonium acetate did not give any better result; see result marked "Experiment 50."

The Effect of Fluorine.—The presence of a fluoride in a solution from which it is attempted to separate aluminum by this method is as disastrous to the results as is the presence of sulphates. From solutions containing phosphates, chloride, and small amounts of sulphates of aluminum, iron, magnesia, lime and soda, and fluoride, the results below are obtained:

			Fluorine present. Mgs.	Alumina. Theory. Mgs.	Alumina. Found. Mgs.
a	2 precipitation		50	39.9	28.4
b	2 "		50	....	27.4
c	2 "		50	19.9	8.9
d	1 "		250	36.9	31.6
e	2 "		250	....	28.5
f	2 "	1st 10 cc. CH_3COONa	....	....	25.3
g	2 "	" " "	"	19.9	14.9
h	2 "	" " "	"	39.9	31.0
i	2 "	" " "	"	19.9	16.6

In none of the current methods is the presence of fluorine mentioned as a disturbing factor. Several determinations by the acetate method, both single and double precipitation in the presence of dissolved calcium fluoride, showed that it has no effect.

Experiment.	CaF_2 present. Mgs.	Alumina. Theory. Mgs.	Alumina. Found. Mgs.
60*a*	250	39.9	40.9
60*b*	250	...	38.1
60*c*	125	19.9	19.4
60*d*	125	...	19.8

The Effect of Manganese, with solutions containing :

	Gram.
Aluminum sulphate	0.25
Calcium phosphate	0.5
Ammonium ferrous alum	0.25
Magnesium chloride	0.10
Manganese chloride	0.10

The following data were obtained :

	Alumina.	
Experiment.	Theory. Mgs.	Found. Mgs.
64*a*	39.9	40.5
64*b*	....	40.3

The work so far done shows that alumina can be quantitatively separated as phosphate from a hydrochloric acid solution containing aluminum, iron, manganese, lime, magnesium, sodium, and potassium, when only small quantities of sulphate are present, and that the presence of silica in the solution produces a plus error too large to be neglected, and that the presence of large quantities of sulphates or the presence of fluorides prevents the complete precipitation of aluminum phosphate. Therefore, to obtain accurate results, silica and fluorine must be removed while sulphates, not more than the equivalent of 1.25 grams of sulphuric acid, may be present.

The following method for alumina in phosphates is based upon the results of these experiments : Treat 1 gram of substance in a platinum dish with from 5 to 10 cc. hydrofluoric acid, let stand in the cold from two to three hours, heat on the water-bath to complete dryness, add 2 cc. concentrated sulphuric acid, running well around the sides, and heat at a low temperature until the substance no longer flows in the dish. By this process fluorine is completely expelled. Cool and add from 10 to 20 cc. concentrated hydrochloric acid, and warm a few minutes to soften the mass; transfer to a small beaker, and boil until all aluminum compounds are surely dissolved (fifteen to thirty minutes); filter from undissolved residue, if any, washing the filter thoroughly, add 50 cc. 25 per cent. ammonium chloride solution and ammonia until alkaline, then hydrochloric acid until the precipitate just dissolves. Cool, dilute to about 250 cc., and add 50 per

cent. sodium thiosulphate solution, drop by drop, until the solution is colorless, adding in all 20 cc.; cover with a watch-glass, boil half an hour, filter, wash back into the same beaker, and dissolve in boiling hydrochloric acid; reprecipitate exactly as before, after adding 2 cc. of a 10 per cent. ammonium phosphate solution. Wash twenty times with 5 per cent. ammonium nitrate solution, and ignite to constant weight. For the second precipitation ammonium thiosulphate may also be used but it is not strictly necessary.

According to the above method from solutions containing :

	Mgs.
Aluminum sulphate	250
Calcium phosphate	500
Ammonium ferrous alum	250
Silica	100
Calcium fluoride	100
Manganese chloride	100
Magnesium chloride	100

These results recorded below were obtained :

	Alumina.	
Experiment.	Theory. Mgs.	Found. Mgs.
63*a*	39.9	40.0
63*b*	....	39.5
63*c*	....	40.1
63*d* (contained fluorine)	....	37.8
63*e*	19.9	19.6
63*f*	....	20.3
65*a*	39.9	39.5
65*b*	....	39.9
66*a* No. 1 ground S. C. rock	17.0 by acetate method	18.4
66*b*	....	17.8
67*a* " 4 " Florida	19.4 " " "	16.3
67*b*	....	14.3

Move the decimal one place to the left to express percentages.

The phosphoric acid was determined in the aluminum phosphate obtained in Experiment No. 63.

	Theory. Mgs.	Found. Mgs.
a	58.2	58.0
b	...	57.6
c	...	57.2

Here, also, the phosphate seems to be the normal, $AlPO_4$, although it was separated in the presence of all substances likely to be found in a natural phosphate, with the exception of silica and fluorine.

The greatest difficulty to be overcome in the execution of this method is the error produced by the presence of fluorine; hence it is necessary to heat the substance for a long time with sulphuric acid to insure the complete removal of fluorine before beginning the separation of the aluminum phosphate.

An attempt to overcome this source of error by adding an alkaline acetate before boiling with thiosulphate gave no better result. In one experiment, however, in which the acetate was added after the boiling, and ten minutes before filtering, all the aluminum phosphate was removed.

The determination of ferric oxide was made as follows: Dissolve 1 gram of substance in 20 cc. sulphuric acid, dilute, filter, washing the filter thoroughly, and if any organic matter is present add a little potassium chlorate and boil until chlorine is expelled. Reduce with zinc, filter, and titrate at once with potassium permanganate solution, 1 cc. of which equals 0.0025 gram ferric oxide.

From solutions used in Experiment 63 I obtained:

	Ferric oxide.	
	Theory. Mgs.	Found. Mgs.
a	51.8	52.5
b	....	52.2
c	....	52.2
d	....	52.2
e	....	51.7
f	....	51.4
No. 1 ground S. C. rock	30.6 by acetate method	29.4
	....	29.3
" 4 " Florida "	14.5	15.4
	....	15.1

I desire to express my thanks to Prof. H. W. Wiley, who assigned this subject for my thesis, and for the valuable assistance given me during the conduct of the work.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WESLEYAN UNIVERSITY.]

THE DISTILLATION OF AMMONIA IN THE DETERMINATION OF NITROGEN.

BY FRANCIS GANO BENEDICT.

Received March 27, 1900.

THE distillation of ammonia in the moist combustion process for determining nitrogen involves the separation of the gaseous ammonia from the alkaline liquid in the distilling flask and the transportation of the gas through a tube into the receiver. While the disengagement of ammonia from a strongly alkaline liquid is readily accomplished by the aid of heat the complete removal of ammonia from the condenser tube is only affected by prolonged boiling to wash the ammonium hydroxide formed out of the tube or by conducting live steam through the tube to vaporize the ammonia which is then driven by the water vapor into the receiver.

The first method is that employed in most laboratories in this country and is designated the "official" method. The second method is that employed in many German laboratories and is here designated the German method.

In the official method the distillation is continued until about 150 cc. of the distillate have been condensed and it is assumed that all the ammonia will have been transferred to the receiver during this operation. The gaseous ammonia coming in contact with the cold water adhering to the inside of the condenser tube dissolves in it forming ammonium hydroxide. The steam generated in the flask condenses in the upper part of the tube and the water formed, slowly runs down, washing out the ammonium hydroxide. It is easily seen that a considerable amount of water would be necessary to insure complete removal of the alkali in this way. Experience has shown that not less than 150 cc. of distillate can safely be relied on to effect this result. This requirement is both expensive and tedious. The operation requires, as a general rule, from forty-five minutes to one hour. Of this time probably not over fifteen to twenty minutes are required to drive all the ammonia out of the liquid, the remaining time being occupied in washing the ammonium hydroxide out of the condenser tube.

According to the German method, the vapors are conducted from the distilling flask through a pipe into the acid, in the receiver with no preliminary cooling, and as a result the contents of the receiver are soon heated to boiling by the latent heat of the steam. Under these conditions, it has been found that after vigorously boiling for twenty minutes all ammonia has been driven out of the alkaline liquid in the distilling flask. Inasmuch as the conditions in this flask are the same in both cases it is only correct to assume that in the official method the ammonia is entirely expelled from the liquid in the same length of time.

Under the conditions existing in the distilling flask by the German method probably no ammonium hydroxide is formed in the condenser tube as the whole system is almost immediately brought to the temperature of steam. Accordingly the gaseous ammonia is carried along mechanically by the water vapor and conducted directly into the receiver.

The great saving in time and gas of this method over the official method is, however, partially offset by the fact that the contents of the receiver at the end of the distillation must be cooled before the titration is made when (as is commonly the case) ammonium hydroxide is used as a standard alkali. Unless the receiver is well cooled, a loss of ammonia is sure to occur.

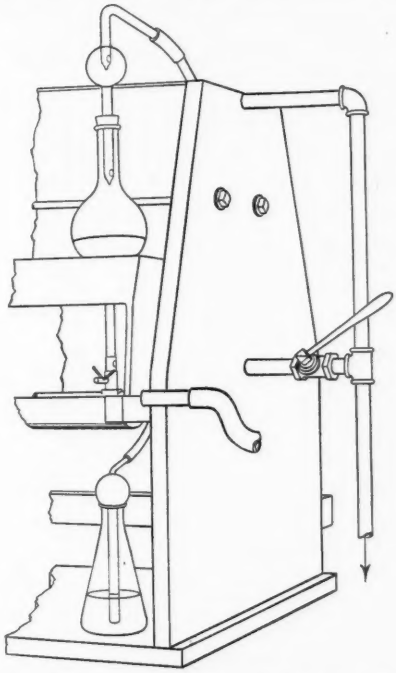
A further objection to the German method lies in the fact that a loss of acid is experienced by the passage of so much steam through the hot liquid in the receiver. This loss should not be neglected in accurate work.

The following modification is, in reality, a combination of the official and the German method, and consists briefly of distilling the liquid into a condenser containing cold water which is allowed to run out a few moments before the end of the distillation that the condenser tubes may become heated. The ammonia in the tubes is then vaporized and driven into the receiver by a current of live steam. By this means the rapid removal of ammonium hydroxide in the condenser tubes is effected without unduly heating the contents of the receiver.

The apparatus which has been in constant use in this laboratory for over a year is shown, in part, in the accompanying figure.

The principal feature is the arrangement of the condenser, a galvanized-iron tank 148 cm. long, 38 cm. deep, and 8 cm. wide.

Ten pieces of block tin pipe 4 mm. internal diameter and 70 cm. long are soldered as usual in the bottom of the tank with ends about 6 cm. long extending through for connection with the receiver and bulb. The upper ends are fastened to one side of



the tank and each is provided with a rubber tube to which a Hopkins'[1] safety distilling bulb is attached.

At one end of the tank and near the bottom a piece of standard half inch pipe is inserted, fitted with a valve or gate which is in turn connected with a ⊤. An overflow is provided near the top of the tank and is connected with the ⊤, the lower arm of which is connected with a sink or drain. The tank which is filled from a water tap at the other end is fastened on a stout frame 35 cm. above the table. The space below is occupied by the receivers and bulb tubes used to prevent back suction of liquid.

[1] This Journal, 18, 227.

With the form of apparatus above described the distillation is carried out as follows: The gas is turned on full and the burners are all lighted.[1] As the liquid in the distilling flask is quite warm from the heat of the dilution of the sulphuric acid and the heat generated by the reaction between the acid and the alkali, the flasks are all vigorously boiling, as a rule, inside of four or five minutes. When all are boiling the time is noted and at the expiration of fifteen minutes the valve is opened, allowing the water to flow out of the condenser. As the water runs out the cold water at the bottom is first withdrawn, the layer of hot water at the top gradually settling and warming the block tin pipes. Just before the layer of hot water begins to flow out the whole condenser tube becomes hot enough to prevent any condensation of water and the live steam blows through the tube into the receiver. This is allowed to continue till the water in the receiver is warmed slightly, the degree of warming being readily determined by occasionally placing the hand on the receiver. As soon as a rise in temperature is perceptible the receiver and bulb are disconnected. This operation requires from four to six minutes after opening the water valve in the apparatus here used. The contents of the flask are therefore vigorously boiling for from nineteen to twenty-two minutes. Repeated tests have shown that all the ammonia is driven off under these conditions. With excessive amounts of ammonia, the boiling operation can be prolonged five minutes before opening the valve. This is seldom necessary, however. Ordinarily, twenty-five to thirty minutes from the lighting of the gas under the flasks to the removal of the receivers suffice to complete the distillation. The titrations can be made immediately.

The length of time necessary to draw off the water in the condenser tank to such a level as to cause live steam to blow through the block tin pipes, is determined by the sizes of the waste pipe and the condenser. With very little experience, it is not difficult to determine how long after boiling the valve should be opened to produce the desired effect at the end of twenty minutes.

The condenser tank here described was not constructed pri-

[1] The use of Jena glass digestion as well as distillation flasks is strongly recommended. With such flasks the full free flame may be employed with impunity. The distillation flasks contain approximately 500 cc. and are about half filled with the alkaline liquid.

marily for this method of distillation. It could undoubtedly be diminished very materially in size with equally satisfactory results.

Obviously the principle is capable of application to numerous forms of condensers. It is only necessary to observe that the flasks are vigorously boiling for at least nineteen or twenty minutes. In a local laboratory the principle has been easily applied to a two-tube condenser constructed out of an old ether can. This apparatus has also given excellent satisfaction for over a year.

MIDDLETOWN, CONNECTICUT.

THE GLUTEN CONSTITUENTS OF WHEAT AND FLOUR AND THEIR RELATION TO BREAD-MAKING QUALITIES.

BY H. A. GUESS.

Received March 22, 1900.

DURING the last eighteen months the writer has been pursuing some investigations in the chemical factors which determine bread-making qualities of wheats and flours, and the notes here submitted, representing some results of the work, are offered as contributions to the chemical literature of an as yet rather neglected subject.

As aids in the work advantage was taken of published notes by other investigators, acknowledgments being more particularly due to the papers of M. E. Fleurent,[1] and of Mr. G. L. Teller.[2]

The result of considerable preliminary work in the estimation of the proteids of both wheats and flours, and subsequent comparisons with results of milling and baking tests, led the writer to confine his attention more particularly to the determination of the gluten constituents gliadin and glutenin, as being apparently the chief determining factors in bread-making qualities.

In the estimation of the gliadin and glutenin, five nitrogenous bodies were considered as being present in the samples,—gliadin,

1 "Sur la composition immédiate du gluten des cereals."—*Compt. rend.*, 123, 327. "Determination of Gluten in Wheat Flour."—Third Congress of Applied Chemistry. Vienna, August, 1898.

2 "Concerning Wheat and its Mill Products: A report of progress of investigations in the chemistry of wheat."—Arkansas Expt. Station, 1898.

glutenin, edestin, leucosin, and the amides. For the separation of the gliadin, alcohol of 0.90 sp. gr. was used, and after deducting the nitrogen of the amides present, the balance of the nitrogen in the alcohol extract, was calculated as gliadin.[1]

The nitrogen of the amides was determined on a separate sample, by extraction with one per cent. salt solution, precipitating all proteids with phosphotungstic acid, and determination of the amide nitrogen in the filtrate.

The edestin and leucosin were separated from the residue from the alcohol extraction, by extraction with one per cent. salt solution, and the nitrogen remaining in the final residue, calculated as glutenin. By making the 1 per cent. salt solution extraction on the residue from the alcohol extract, any uncertainty from partial solubility of gliadin, or allied proteid bodies, in salt solution, was avoided.[2]

The *modus operandi* of the analysis, was as follows:

a. Five grams of the finely ground wheat meal or flour, placed in a 250 cc. flask, 1 per cent. salt solution added from a pipette, at sufficient pressure to prevent any tendency to clot; flask filled to the mark, shaken at intervals for one hour, and let settle for two hours; decanted through a filter, duplicate portions of 100 cc. each of the clear supernatant liquid withdrawn, the proteids precipitated with a few cubic centimeters of 10 per cent. solution of phosphotungstic acid, the precipitate allowed to settle, 50 cc. of the clear filtrate evaporated with sulphuric acid, and the amide nitrogen determined.

b. One gram of sample put in a 500 cc. Kjeldahl flask with 100 cc. alcohol of 0.90 sp. gr., shaken to thoroughly mix, placed on a water-bath, and maintained at a temperature slightly below the boiling-point of the alcohol mixture; agitated every ten minutes for one hour, allowed to settle for one hour and decanted into a similar flask, being careful to not carry decantation close enough to cause any turbidity to appear in the decanted filtrate; 25 cc. fresh hot alcohol added, allowed to settle twenty minutes, decanted, and the operation repeated three times. In the extract, the alcohol is distilled off, and the nitro-

[1] *Am. Chem. J.*, 15, 441.
[2] *Ibid.*, 392 *et seq.*

gen in the residue determined, the amide nitrogen (*a*) subtracted, and the balance calculated as gliadin (N × 5.7).

c. To the residue from the alcohol extraction, after cooling, 250 cc. of 1 per cent. salt solution are added; it is allowed to settle for one hour, and decanted through a filter; 250 cc. fresh salt solution are added, shaken at intervals for one hour and allowed to settle for two hours, decanting through the same filter; the filter and contents are added to the residue in the flask, and nitrogen determined and calculated to glutenin.

Following are results of some determinations made in this way on wheats from different elevator points, throughout the Canadian Northwest, giving the locality, the buyer's regular grading mark, the percentages of gliadin and glutenin respectively; the ratio of same, and a composite factor representing this ratio × the total percentage of gluten (gliadin and glutenin) present. Also of the same determinations made at regular intervals on the flours produced from these wheats, by one of the largest milling companies in Canada. Analyses of the different 'break' products of the mill were also similarly made, but are not here included.

This ratio of gliadin to glutenin has been used tentatively, as an index of the gluten quality. So far as the writer has been enabled to have this index checked by actual baking tests on the flour produced, it was found that the elastic quality of the gluten was improved in proportion as the ratio of gliadin to glutenin increased, and as yet no limit has been found beyond which further increase of gliadin ratio rendered the gluten inelastic or sticky.

Manifestly, if this ratio of gliadin to glutenin be a true index of the quality of the gluten, the factor of quantity must also be taken account of in estimating the true gluten value of a wheat or flour, the value being the total number of units of gluten present × the value per unit. Need was felt, in the work, for a factor to indicate this gluten value, so as to be of use commercially, in grading wheats and flours, and in the lists following this gluten value is in each case calculated out as a composite factor made up of the percentage of gluten × ratio of gliadin to glutenin (quality index).

CANADIAN NORTHWEST WHEATS.

Locality.	Buyer's grade.[1]	Gliadin. Per cent.	Glutenin. Per cent.	Ratio of Gliadin to Glutenin.	Composite factor. Gluten ratio. Per cent.
Reston	2 H	7.32	4.43	1.65	19.38
Plum Coulee ..	1 N	5.4	3.61	1.49	13.42
Carman	1 H	7.77	3.30	2.34	25.90
Holland.....	2 H	5.73	4.0	1.43	13.91
Lauder.....	2 H	7.18	4.67	1.53	18.13
Virden (damp)	1 H	5.19	4.93	1.05	10.62
Lauder '97	1 H	8.39	4.61	1.8	23.4
Franklin	1 N	6.14	4.53	1.35	14.40
Hartney.....	1 H	5.43	4.24	1.2	11.6
Dom. City.....	2 N	5.15	3.71	1.38	12.22
McDonald.....	1 N	5.51	5.08	1.08	11.43
Manitou	2 N	4.57	5.91	0.7	7.33
Altonia.....	1 H	6.53	4.25	1.54	16.60
Reston	1 H	7.7	4.88	1.57	19.75
Treesbank.....	1 H	7.36	5.0	1.47	18.16
Douglass.....	1 H	7.7	4.4	1.77	21.41
Qu'appelle	1 H	7.86	4.16	1.9	22.84
Souris	1 H	7.01	5.10	1.37	16.59
Indian Head ..	1 H	7.98	4.92	1.62	20.89
Sintaluta.....	1 H	8.14	5.2	1.56	20.81
Whitewater ...	1 H	6.12	5.44	1.12	12.95
Boissevain	1 H	6.46	4.84	1.33	15.02
Stocton	1 H	6.62	4.40	1.5	16.53
Rosenfeldt	1 H	5.14	5.04	1.0	10.18
Ninga.....	2 H	5.59	5.0	1.11	11.97
McGregor.....	1 N	6.02	4.88	1.23	13.40
Neepawa	1 N	4.76	4.64	1.0	9.4
Portage.....	..	6.7	4.92	1.36	15.66
Portage (damp)	..	6.4	6.08	1.05	13.10
Elkhorn	1 H	7.06	5.2	1.35	16.55
Thornhill	1 N	6.5	4.4	1.47	16.02
Fleming	1 H	7.50	5.09	1.47	18.52
Griswald	1 H	7.50	5.64	1.33	17.48
Mileta	1 H	8.18	5.04	1.6	21.15
Bagat	2 H	7.34	5.0	1.47	18.13
Alemeda	1 H	8.29	4.45	1.86	23.69
Stocton	L White Fife	6.6	4.7	1.4	15.82
Sintaluta	1 H	9.21	4.60	2.1	27.62
Methven	1 H	8.52	5.0	1.7	22.98
Elkhorn(damp)	..	8.13	4.64	1.75	22.34
Carroll	..	7.58	5.30	1.43	18.42
Indian Head...	1 H	7.88	4.77	1.65	20.87

[1] Grades in descending. 1 Hard ; 2 Hard ; 1 Northern ; 2 Northern.

Locality.	Buyer's grade.[1]	Gliadin. Per cent.	Glutenin. Per cent.	Ratio of Gliadin to Glutenin.	Composite factor. Gluten ratio. Per cent.
Arden	1 N	5.07	5.49	0.92	9.71
Treesbank	1 H	8.76	4.82	1.81	24.57
Alemeda	1 White Fife	8.85	4.6	1.92	25.82
McGregor	2 H	6.44	4.36	1.47	15.87
Dauphin	1 N	4.25	4.25	1.0	8.5
Morden	1 N	3.65	3.65	1.0	7.3
Gretna	1 N	3.8	3.7	1.0	7.5
McDonald	2 H	5.8	4.0	1.45	13.21
Carberry	1 N	5.7	3.7	1.53	14.38
Moosomin	1 H	7.65	4.0	1.9	22.13
Treesbank	1 H	7.87	4.3	1.83	22.47
Neepawa	1 N	6.65	4.2	1.57	17.03
Indian Head	1 H	6.35	4.1	1.51	16.48
Carroll	1 H	6.7	4.1	1.63	17.60
Elva	2 H	7.6	3.95	1.92	22.17
Winkler	1 N	6.0	3.5	1.71	16.24
Altonia	1 N	7.5	4.1	1.82	21.11
Dom. City	2 N	5.4	3.7	1.46	13.28
Elkhorn (damp)	..	6.5	4.0	1.65	18.00
Elva	2 H	8.37	4.3	1.94	24.58
Reston	2 H	8.0	4.5	1.78	22.25
Douglass (damp)	..	6.65	4.2	1.58	17.13
Sintaluta	1 H	7.77	4.5	1.73	21.2
Boissevain	1 H	7.3	4.4	1.65	19.3
Qu'appelle	1 H	8.58	4.2	2.904	26.0
Manitou	2 Spring	4.0	4.2	0.95	7.78
Bagat	1 N	3.7	4.0	0.93	7.20
McGregor	1 N	4.65	4.10	1.1	9.62
Thornhill	1 N	5.4	4.2	1.3	12.48
Hamiota	1 H	7.15	4.6	1.54	18.10
Hartney	1 H	7.8	4.0	1.95	23.0
Treesbank	..	8.37	4.0	2.09	25.85
Indian head	..	7.51	4.1	1.83	21.24
Carman	..	7.77	3.6	2.14	24.18
Douglass	..	7.8	3.8	2.0	23.2
Bagat	..	7.0	4.2	1.66	18.59
Holland	..	6.1	4.4	1.4	14.7
Methven	..	8.1	4.0	2.02	24.44

[1] Grades, in descending order : 1 Hard ; 2 Hard ; 1 Northern ; 2 Northern.

CANADIAN NORTHWEST AND OTHER FLOURS.

Name of flour.	Grade.[1]	Gliadin. Per cent.	Glutenin. Per cent.	Ratio of gliadin to glutenin.	Composite factor. Per cent. gluten × ratio.
Keewatin	Patent	8.13	2.24	3.62	37.54
"	Baker's	8.47	3.90	2.17	26.84
"	Algoma	7.98	4.55	1.75	21.92
"	Glenwood	7.2	5.53	1.3	16.54
Portage	Patent	8.4	2.1	4.0	42.00
"	Baker's	8.65	2.6	3.32	37.25
"	Algoma	8.2	3.2	2.59	29.78
"	Glenwood	8.0	4.7	1.7	21.69
Keewatin	Patent	8.9	1.60	5.56	58.38
"	Baker's	8.14	3.52	2.3	26.81
"	Algoma	7.46	4.80	1.6	19.61
"	Glenwood	6.90	5.90	1.2	15.38
Austria-Hungary (best)		9.38	2.80	3.35	40.80
Keewatin	Patent	8.25	2.0	4.12	42.23
"	Baker's	9.06	2.25	4.02	45.46
"	Algoma	8.63	3.24	2.66	31.57
"	Patent	9.0	1.9	4.73	51.55
"	Baker's	8.65	3.2	2.7	32.0
"	Algoma	8.5	3.8	2.23	27.42
"	Glenwood	8.1	4.9	1.65	21.45
"	Patent	7.95	2.85	2.78	30.02
"	Baker's	8.1	3.1	2.61	29.23
Ogilvie	Patent	8.04	2.92	2.76	30.24
"	Baker's	7.4	3.6	2.05	22.55

At the present stage of progress in these investigations, it cannot be stated that these ratios, or the calculated factors, are true indices of the bread-making qualities and values of the different wheats and flours, but it is certain that there is a direct and very intimate connection between the same.

The subject is one worthy of attention by industrial chemists, and it is quite possible that in time the buying, mixing, and milling of wheats may come under as definite chemical control as are, at present, similar operations, with respect to the smelting of ores.

LABORATORY OF THE OTTAWA GOLD MILLING AND MINING CO., KEEWATIN, ONTARIO, March 6, 1900.

[1] Grades in descending scale: Patent, Baker's, Algoma, Glenwood.

LIME AND SULPHURIC ACID BY THE PHOTOMETRIC METHOD.

By J. I. D. Hinds.

Received March 30, 1900.

IN this Journal, **18**, 661, I gave the results of some investigations looking to the rapid determination of lime and sulphuric acid by means of the opacity of the precipitates produced in the usual way. Since then I have had occasion to make frequent tests of the accuracy of the method and am able to give some interesting results.

The only apparatus needed is the photometric cylinder made of glass. It is 3.5 centimeters wide and 20 centimeters high, and is graduated in centimeters and millimeters from the inside of the bottom for the convenient reading of the depth of the liquid in the cylinder. It is used with an ordinary sperm or wax candle. The cylinder is held over the lighted candle and the water containing the precipitate is poured into the cylinder until the image of the flame just disappears. The depth is read and the per cent. is calculated from the equation or read from a table. The lime is precipitated with solid calcium oxalate and the sulphuric acid with solid barium chloride. The equations used are as follows:

$$\text{For } CaCO_3,\ y = \frac{0.0642}{x - 0.3}; \qquad \text{For } CaO,\ y = \frac{0.0360}{x - 0.3};$$

$$\text{For } H_2SO_4,\ y = \frac{0.0590}{x}; \qquad \text{For } SO_3,\ y = \frac{0.0482}{x};$$

in which x is the reading of the cylinder and y the per cent. sought. For the details of the method, see the article above referred to. A table computed from these equations is appended to this article.

Near the university building in Lebanon is a bored well yielding a limestone water, analysis of which shows that it contains among other things

Calcium carbonate	about	16.00 parts in	100,000
Magnesium "	"	13.00 " "	100,000
Magnesium sulphate "		16.00 " "	100,000
Total solids		60.80 " "	100,000

I made a series of photometric and gravimetric determinations of the lime and sulphuric acid in this water from day to day, with the following results:

Calcium carbonate—parts in 100,000.

	1.	2.	3.	4.	5.	6.	7.
Photometric	16.5	15.7	15.7	16.5	15.7	22.2	19.5
Gravimetric	16.4	16.0	15.5	16.0	15.5	22.4	19.0
Difference	0.1	0.3	0.2	0.5	0.2	0.2	0.5

Sulphuric acid—parts in 100,000.

	1.	2.	3.	4.	5.
Photometric	13.1	11.8	5.7	7.9	4.9
Gravimetric	13.2	11.4	5.4	7.2	4.7
Difference	0.1	0.4	0.3	0.7	0.2

These differences, omitting the decimal point, mean parts in a million of the water and are a reasonably small fraction of the total amount present. For sanitary and technical purposes the photometric determinations are just as good as those made in the regular way. When we consider that one of these determinations can be made in five minutes and that the method is adapted to many other substances, it seems to be worthy of the attention and careful investigation of chemists. It is much more accurate than many of the approximate methods now in use and requires no previous preparation in the way of standard solutions.

I have found the method practicable in the determination of the lime in carbonates. I give one example. A sample of clayey limestone containing 16.14 per cent. of calcium carbonate gave by this method 16.46 per cent. The determination was made as follows: Dissolved 0.1081 gram of the limestone in hydrochloric acid with a few drops of nitric acid, evaporated to dryness in a porcelain dish over a free flame, added water with a little hydrochloric acid, filtered, neutralized with ammonia, made up to 150 cc., then tested in the usual way. The reading in the cylinder was 6.0 cm. Substituting this for x in the equation we find the solution to contain 0.0112 per cent. of calcium carbonate. The calculation is then made as follows:

100 cc. contain 0.0112 gram $CaCO_3$.
150 " " 0.0178 " "

0.1081 gram of the sample contains 0.0178 gram $CaCO_3$, or

16.46 per cent. The whole operation can be performed within a half hour.

The determination of sulphuric acid in urine is very easy and rapid. Five or ten cc. of the urine are measured from a burette or pipette, made slightly acid with hydrochloric acid, and diluted to 100 cc. Barium chloride is added and the reading taken. Two trials with a urine diluted from 10 to 100 cc. gave the same reading; *viz.*, 3.0 cm. This corresponds to 0.0197 per cent. H_2SO_4. Multiplying by 10 we have 0.197 as the per cent. of H_2SO_4 in the urine.

To save the trouble and labor of computation I have prepared the accompanying table from which the percentages can be directly taken as soon as the reading is made.

TABLE FOR PHOTOMETRIC DETERMINATION OF LIME AND SULPHURIC ACID.

y equals the per cent. desired, and x is the reading of cylinder in centimeters. For parts in 100,000 remove the decimal point three places to the right.

x.	Per cent. $CaCO_3$. $y = \frac{0.0642}{x-0.3}$.	Per cent. CaO. $y = \frac{0.0360}{x-0.3}$.	Per cent. H_2SO_4. $y = \frac{0.0590}{x}$.	Per cent. SO_3. $y = \frac{0.0482}{x}$.
1.0	0.0917	0.0514	0.0590	0.0482
1.1	0.0802	0.0450	0.0536	0.0438
1.2	0.0713	0.0400	0.0492	0.0402
1.3	0.0642	0.0360	0.0454	0.0371
1.4	0.0583	0.0327	0.0421	0.0344
1.5	0.0534	0.0300	0.0393	0.0322
1.6	0.0494	0.0277	0.0370	0.0301
1.7	0.0456	0.0257	0.0347	0.0283
1.8	0.0428	0.0240	0.0328	0.0268
1.9	0.0401	0.0225	0.0311	0.0254
2.0	0.0377	0.0212	0.0295	0.0241
2.1	0.0356	0.0201	0.0281	0.0230
2.2	0.0338	0.0190	0.0268	0.0219
2.3	0.0321	0.0180	0.0257	0.0210
2.4	0.0306	0.0172	0.0246	0.0201
2.5	0.0292	0.0164	0.0236	0.0193
2.6	0.0279	0.0156	0.0227	0.0185
2.7	0.0268	0.0150	0.0218	0.0179
2.8	0.0257	0.0144	0.0211	0.0172
2.9	0.0247	0.0138	0.0203	0.0166
3.0	0.0238	0.0133	0.0197	0.0161
3.1	0.0229	0.0129	0.0190	0.0156
3.2	0.0221	0.0124	0.0184	0.0151

x.	Per cent. $CaCO_3$. $y = \frac{0.0642}{x - 0.3}$.	Per cent. CaO. $y = \frac{0.0360}{x - 0.3}$.	Per cent. H_2SO_4. $y = \frac{0.0590}{x}$.	Per cent. SO_3. $y = \frac{0.0482}{x}$.
3.3	0.0214	0.0120	0.0179	0.0146
3.4	0.0207	0.0116	0.0174	0.0142
3.5	0.0201	0.0112	0.0169	0.0138
3.6	0.0195	0.0109	0.0164	0.0134
3.7	0.0189	0.0106	0.0159	0.0130
3.8	0.0183	0.0103	0.0155	0.0127
3.9	0.0178	0.0100	0.0151	0.0124
4.0	0.0173	0.0097	0.0147	0.0121
4.1	0.0169	0.00947	0.0144	0.0118
4.2	0.0165	0.00923	0.0141	0.0115
4.3	0.0161	0.00900	0.0137	0.0112
4.4	0.0157	0.00878	0.0134	0.0110
4.5	0.0153	0.00857	0.0131	0.0107
4.6	0.0149	0.00837	0.0128	0.0105
4.7	0.0146	0.00818	0.0125	0.0103
4.8	0.0143	0.00800	0.0123	0.0101
4.9	0.0140	0.00782	0.0120	0.00983
5.0	0.0137	0.00766	0.0118	0.00964
5.1	0.0134	0.00750	0.0116	0.00945
5.2	0.0131	0.00735	0.0113	0.00927
5.3	0.0128	0.00720	0.0111	0.00909
5.4	0.0126	0.00706	0.0109	0.00992
5.5	0.0123	0.00692	0.0107	0.00876
5.6	0.0121	0.00679	0.0105	0.00861
5.7	0.0119	0.00667	0.0104	0.00845
5.8	0.0117	0.00654	0.0102	0.00831
5.9	0.0115	0.00643	0.0100	0.00817
6.0	0.0113	0.00632	0.00983	0.00804
6.1	0.0111	0.00621	0.00967	0.00790
6.2	0.0109	0.00610	0.00952	0.00777
6.3	0.0107	0.00600	0.00937	0.00765
6.4	0.0105	0.00590	0.00922	0.00753
6.5	0.0104	0.00580	0.00908	0.00742
6.6	0.0102	0.00571	0.00894	0.00730
6.7	0.01003	0.00562	0.00881	0.00719
6.8	0.00988	0.00554	0.00868	0.00709
6.9	0.00973	0.00545	0.00855	0.00698
7.0	0.00958	0.00537	0.00843	0.00689
7.1	0.00944	0.00529	0.00831	0.00679
7.2	0.00930	0.00522	0.00820	0.00669
7.3	0.00917	0.00514	0.00808	0.00660
7.4	0.00904	0.00507	0.00797	0.00651
7.5	0.00892	0.00500	0.00787	0.00642
7.6	0.00879	0.00493	0.00776	0.00634

x.	Per cent. $CaCO_3$. $y = \frac{0.0642}{x - 0.3}$.	Per cent. CaO. $y = \frac{0.0360}{x - 0.3}$.	Per cent. H_2SO_4. $y = \frac{0.0590}{x}$.	Per cent. SO_3. $y = \frac{0.0482}{x}$.
7.7	0.00867	0.00486	0.00766	0.00626
7.8	0.00856	0.00480	0.00756	0.00618
7.9	0.00845	0.00474	0.00747	0.00610
8.0	0.00834	0.00468	0.00737	0.00602
8.1	0.00823	0.00462	0.00728	0.00595
8.2	0.00813	0.00456	0.00720	0.00588
8.3	0.00802	0.00450	0.00711	0.00581
8.4	0.00792	0.00444	0.00702	0.00574
8.5	0.00783	0.00439	0.00694	0.00567
8.6	0.00773	0.00434	0.00686	0.00560
8.7	0.00764	0.00429	0.00678	0.00554
8.8	0.00755	0.00424	0.00670	0.00548
8.9	0.00746	0.00419	0.00663	0.00541
9.0	0.00738	0.00414	0.00655	0.00536
9.1	0.00730	0.00409	0.00648	0.00530
9.2	0.00721	0.00404	0.00641	0.00524
9.3	0.00713	0.00400	0.00634	0.00518
9.4	0.00705	0.00396	0.00628	0.00513
9.5	0.00698	0.00391	0.00621	0.00507
9.6	0.00690	0.00387	0.00615	0.00502
9.7	0.00683	0.00383	0.00608	0.00497
9.8	0.00676	0.00379	0.00602	0.00492
9.9	0.00669	0.00375	0.00596	0.00487
10.0	0.00662	0.00371	0.00590	0.00482
10.1	0.00655	0.00367	0.00584	0.00477
10.2	0.00648	0.00364	0.00578	0.00473
10.3	0.00642	0.00360	0.00573	0.00468
10.4	0.00636	0.00357	0.00567	0.00463
10.5	0.00629	0.00353	0.00562	0.00459
10.6	0.00623	0.00350	0.00557	0.00455
10.7	0.00617	0.00346	0.00551	0.00451
10.8	0.00611	0.00343	0.00546	0.00447
10.9	0.00606	0.00340	0.00541	0.00442
11.0	0.00600	0.00336	0.00536	0.00438
11.1	0.00594	0.00333	0.00532	0.00434
11.2	0.00589	0.00330	0.00528	0.00430
11.3	0.00584	0.00327	0.00523	0.00426
11.4	0.00578	0.00324	0.00518	0.00423
11.5	0.00573	0.00321	0.00513	0.00419
11.6	0.00568	0.00318	0.00508	0.00415
11.7	0.00563	0.00316	0.00504	0.00412
11.8	0.00558	0.00313	0.00500	0.00408
11.9	0.00553	0.00310	0.00496	0.00405
12.0	0.00548	0.00308	0.00492	0.00401

x.	Per cent. $CaCO_3$. $y=\frac{0.0642}{x-0.3}$.	Per cent. CaO. $y=\frac{0.0360}{x-0.3}$.	Per cent. H_2SO_4. $y=\frac{0.0590}{x}$.	Per cent. SO_3. $y=\frac{0.0482}{x}$.
12.1	0.00543	0.00305	0.00488	0.00398
12.2	0.00539	0.00303	0.00484	0.00395
12.3	0.00535	0.00300	0.00480	0.00392
12.4	0.00531	0.00298	0.00476	0.00389
12.5	0.00526	0.00295	0.00472	0.00386
12.6	0.00522	0.00293	0.00468	0.00383
12.7	0.00517	0.00290	0.00465	0.00380
12.8	0.00513	0.00288	0.00461	0.00377
12.9	0.00509	0.00285	0.00457	0.00374
13.0	0.00505	0.00283	0.00454	0.00371
13.2	0.00498	0.00279	0.00447	0.00364
13.4	0.00490	0.00275	0.00440	0.00359
13.6	0.00483	0.00271	0.00434	0.00354
13.8	0.00476	0.00267	0.00427	0.00349
14.0	0.00469	0.00263	0.00421	0.00344
14.2	0.00462	0.00259	0.00415	0.00339
14.4	0.00455	0.00255	0.00410	0.00335
14.6	0.00449	0.00251	0.00404	0.00330
14.8	0.00443	0.00248	0.00399	0.00326
15.0	0.00437	0.00245	0.00393	0.00321
15.5	0.00422	0.00237	0.00381	0.00311
16.0	0.00409	0.00229	0.00369	0.00301
16.5	0.00396	0.00222	0.00358	0.00292
17.0	0.00384	0.00216	0.00347	0.00284
17.5	0.00373	0.00209	0.00337	0.00276
18.0	0.00363	0.00203	0.00328	0.00268
18.5	0.00353	0.00198	0.00319	0.00261
19.0	0.00343	0.00192	0.00311	0.00254
19.5	0.00334	0.00187	0.00303	0.00247
20.0	0.00326	0.00183	0.00295	0.00241

UNIVERSITY OF NASHVILLE.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 22.]

UPON BISMUTH COBALTICYANIDE.

BY J. A. MATHEWS.

Received April 28, 1900.

IN a recent article entitled "A Preliminary Study of the Cobalticyanides,"[1] by E. H. Miller and myself, mention was made of bismuth cobalticyanide. It was stated that "the original precipitate seems to be a normal cobalticyanide, but it has not been analyzed and no mention of such a compound is found in the

[1] This Journal, **22**, 65 (1900).

literature." It was further stated that as lead cobalticyanide is exceedingly soluble in water, there might be a possibility of effecting a separation of bismuth from lead in pig-leads by the use of potassium cobalticyanide. I have analyzed the cobalticyanide of bismuth, noted carefully its properties, and determined the most favorable conditions for its precipitation. The results have not been favorable to its use in the analysis of pig-leads but it may still be found useful in the analysis of lead-bismuth alloys, "fusible metals" such as Wood's alloy, etc.

The precipitate of bismuth cobalticyanide is crystalline, settles and filters well, and contains more or less water which is not completely given up below 165° C. The anhydrous compound has the formula $BiCo(CN)_6$. The theoretical percentage of bismuth for this compound is 49.17. The average of three determinations gave 49.05 per cent. bismuth. When freshly precipitated and before filtering, the precipitate appears white but on the filter it has a slight greenish tint. During the process of dehydrating the color becomes blue, getting darker as the temperature rises; then upon exposure to the air it reabsorbs water rapidly and the color becomes pink. This behavior seems to indicate some decomposition of the cobalticyanide radical at the temperature required for complete dehydration, and this view is strengthened by the fact that different samples exhibit differences of tint and that, in general, after exposing the anhydrous samples to the air, the depth of the pink tint is proportional to the depth of blue in the sample exposed.

A sample of bismuth cobalticyanide dried below 100° C. and exposed to the air for one week, lost by subsequent heating to 162° C., 19.5 per cent. Two portions dried to constant weight at 100° C. lost, by heating to 165° C., 4.35 per cent. and 4.24 per cent. respectively, corresponding to one molecule of water. The samples upon exposure to the air reabsorbed about 16.25 per cent. of water, the actual percentage fluctuating slightly from day to day.

Completeness of the Precipitation.—By means of several series of experiments in which bismuth solutions were precipitated by potassium cobalticyanide, it was found that below a concentration of 0.0079 gram of bismuth per cubic centimeter the precipitate was under no conditions complete and that at ten times

that dilution no precipitate was produced even on long standing. By varying the ratio of bismuth to potassium cobalticyanide, it was shown that a decided excess of the latter was beneficial. The precipitation is found to be more complete if acetic acid is present. Boiling assists in the precipitation of very dilute solutions, but a solution so dilute that no precipitate forms in the cold is never completely precipitated by heating. The solubility of the precipitate does not vary much with change of temperature, and when once formed is not soluble in a quantity of water which would have prevented its formation in the beginning.

The following tables, with the remarks accompanying each, show the influence of different conditions upon the completeness of precipitation. A solution containing 0.0794 gram of bismuth per cubic centimeter in nitric acid was used in all cases.

I. VARYING RATIO OF $Bi(NO_3)_3$ TO $K_3Co(CN)_6$.

	Temperature.	$Bi(NO_3)_3$. cc.	Half-normal $K_3Co(CN)_6$. cc.
1	cold	5	15
2	"	3	15
3	"	1	15
4	hot	5	15
5	"	3	15
6	"	1	15

All filtrates showed a trace of bismuth with $(NH_4)_2S$: Greater in 4, 5, and 6, than in 1, 2, and 3; deepest in 1 and 4; least in 3 and 6, respectively. The insolubility is therefore increased by an excess of $K_3Co(CN)_6$.

II. VARYING VOLUME. RATIO OF $Bi(NO_3)_3 : K_3Co(CN)_6$ CONSTANT.

	$Bi(NO_3)_3$. cc.	H_2O. cc.	$K_3Co(CN)_6$. cc.
1	5	5	15
2	3	7	9
3	1	9 $(+H\overline{A})$	3 also,
[4	1	9	6]

Number 3 is very incomplete. Filtrate gave large precipitate with ammonium carbonate. 1, 2, and 4 showed only a trace of bismuth with $(NH_4)_2S$. Comparison of 3 and 4 shows the effect of increasing the amount of $K_3Co(CN)_6$.

III. CONSTANT VOLUME.

	$Bi(NO_3)_3$. cc.	$H_2O(+HA)$. cc.	$K_3Co(CN)_6$. cc.
1	5	5	15
2	3	12	10
3	1	19	5
4	1	21	3

In 1, 2, and 3 the ratio of $K_3Co(CN)_6$ to $Bi(NO_3)_3$ increases with the dilution. Filtrate from 3 contained 10 per cent. of the bismuth; filtrate from 4 contained 57 per cent. of the bismuth. In 1 and 2, the filtrates showed a trace of bismuth with $(NH_4)_2S$, greater in 2 than in 1, showing that the completeness of the precipitation increases with the concentration.

A RAPID METHOD FOR THE DETERMINATION OF CARBON IN IRON OR STEEL BY COMBUSTION.

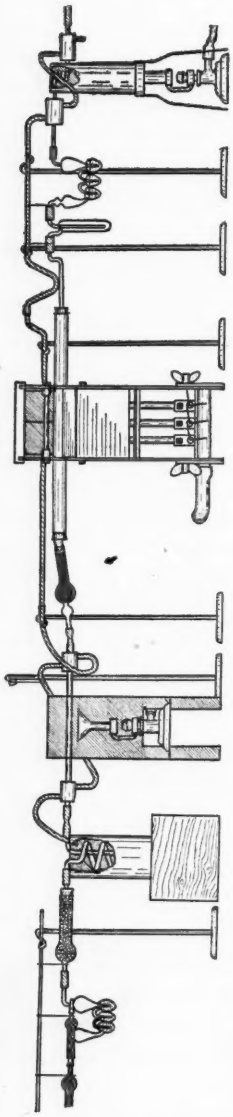
BY GEO. WM. SARGENT.

Received April 5, 1900.

THE part taken by the carbon in determining the utility of steel or iron, especially the effect of slight changes in the quantity, impresses one with the need of exercising the greatest care that its estimation may be accurately made, and yet the large number of determinations required in a limited time calls for greater speed in their accomplishment.

The color method of Eggertz is probably the most rapid, but its application is so limited that it is scarcely used outside of regular furnace work where straight steels only are encountered, and the steel has undergone the same treatment, consequently the carbon is present in always the same condition. The advent of alloys of nickel, chromium, tungsten, molybdenum, titanium, etc., with iron, forces even the furnace chemist back to the most reliable method,—that of the combustion, in oxygen, of the carbon residue from the solution of the drillings. During the past three months the results obtained in this laboratory, by this method somewhat modified, have been so eminently gratifying with regard to accuracy, rapidity, and simplicity of the apparatus used, that I believe it worthy the attention of other chemists.

The apparatus as shown by the accompanying cut consists of, beginning on the right, a small copper or platinum spiral, water-jacketed at each end to prevent the burning of the rubber con-



nections, and suspended in a copper cylinder over a burner; a Geissler potash bulb, followed by an empty "safety" tube, then the porcelain tube resting in a three-burner combustion furnace; a glass tube filled with coarse, wet sand; a copper tube filled with copper oxide and also water-jacketed at each end; a tin can containing a copper worm; then a 6-inch calcium chloride tube; the weighed potash bulb and its calcium chloride tube; and finally the guard.

It will be best to describe in detail each portion of the apparatus and its function.

The spiral is made from a platinum tube 17 inches long and $\frac{5}{32}$ inch in diameter. This gives four close coils $\frac{3}{4}$ inch in diameter and leaves 4 inches extend on either side. The water-jackets are two pieces of $\frac{1}{2}$ inch copper tubing $1\frac{1}{2}$ inches long, closed at the ends by rivet burrs, carefully soldered and containing an outlet and an inlet, the outlet of the one being connected to the inlet of the other by a $\frac{1}{4}$ inch copper tube bent around the support. The latter is a $1\frac{1}{2}$ inch copper tube with $\frac{1}{16}$ inch walls, 6 inches long, resting on three legs sufficiently long to bring the spiral the proper distance from the burner. A two-way cock leads the oxygen or air from the tanks to the spiral where any hydrocarbons are burned. The resulting carbon dioxide is caught in the Geissler potash bulb to which the spiral is connected by rubber tubing, thence the purified oxygen or air passes through the empty tube which is used to catch any potassium hydroxide from the Geissler bulb, into the combustion tube. Both the potash

bulb and the "safety" are suspended from the small copper pipe conveying the water from the outlet of the second water-jacket to the first jacket on the copper oxide tube. The combustion tube is a $\frac{5}{8}$ inch glazed porcelain tube 16 inches long, 5 inches of which extend on either side of the combustion furnace. The curved piece of fire-brick protects the tube from direct contact with the flames of the furnace. The latter is 5 inches long, having but 3 burners and was made from an old 10-burner furnace. To prevent the boat holding the carbon from being pushed into the combustion tube beyond the heated portion, a piece of clay pipe stem is placed at one end. The gases from the combustion tube pass through the coarse, wet sand loosely packed in a $\frac{1}{2}$ inch glass tube 6 inches long and held in place by two small disks of copper gauze placed at either end. This moist sand and the copper disks effectually hold any hydrochloric acid or chlorine that the gases may contain. The copper oxide tube is a straight piece of copper $\frac{3}{8}$ inch in diameter, 1 foot long, water-jacketed at each end, the water flowing from the outlet of the first jacket to the second, and thence into the tin can containing the worm. The copper oxide tube rests on a support of sheet tin, bent as shown in the cut, and slit at each side and at the bottom of the back, the two side openings supporting the copper tube, while the one in the back allows the gas pipe to enter to the burner, which has a spreader so that the copper oxide is heated for a distance of at least 3 inches. The worm consists of 3 very loose coils of $\frac{1}{4}$ inch copper tubing. A piece of tube about 20 inches long will make about the right size worm. From the cooler, the gases are dried by passing through 6 inches of thoroughly dehydrated calcium chloride. They then enter the weighed potash bulb and its calcium chloride tube, which are in one piece. These bulbs are extra large at the part holding the potash solution, being 1 inch long and $\frac{3}{4}$ inch wide, weighing, when filled for use, about 75 grams, and holding 30 cc. caustic potash solution. They, therefore, allow the gases to come in contact with more of the solution for a longer time.[1] The guard tube is the usual calcium chloride tube.

It is absolutely essential that all the calcium chloride used should be thoroughly dehydrated, that none of the fine powder

[1] These bulbs were made to order by Queen & Co., Philadelphia.

be placed in the tubes, particularly that one attached to the weighed potash bulb, and that as little of the space within the tubes as is possible be taken up with cotton, which does no good as an absorbent. It is best to sift out the fine powder from the dehydrated calcium chloride and take that which is about $\frac{3}{16}$ inch diameter, or the size of a dried pea.

The apparatus being ready, the combustion is proceeded with as follows:

A stream of water is started through the water-jackets, the burners under the spiral and copper oxide lighted, also the 3 burners of the furnace, which are regulated so the tips of the flames just touch the curved fire-brick upon which the porcelain tube rests. After ten minutes the burners may be turned on sufficiently far to bring that part of the tube within the furnace to a red heat and hold it there. The water overflowing from the can should be about 15° C. The weighed potash bulb having been connected, a current of air is started through the apparatus at the rate of about 5 bubbles per second in the weighed bulb (this is a little faster than one can count), the stopper at the forward end of the combustion tube is withdrawn and, as quickly as possible, the platinum boat containing the carbon residue obtained by the standard method of solution of steel, is pushed into the tube until it meets the pipe stem, and the stopper immediately replaced. The air is then turned off and replaced by a current of oxygen at a slightly slower rate of speed, about $4\frac{1}{2}$ bubbles per second. At the expiration of ten minutes the oxygen is turned off and the air on at the former speed for ten minutes. The connections are then broken, a new weighed potash bulb placed in the train; a fresh boat containing the carbon is inserted after removing the first one and a new combustion proceeded with. The boats should be taken from the oven, which is kept at 100° C., and at once put into the porcelain tube in order to prevent a cold boat cracking the tube.

The copper oxide is always kept at a red heat, as is also the combustion tube, as long as the apparatus is in use, from the beginning of the day's work until its completion.

A combustion is thus made in twenty minutes, and one man, with two of these pieces of apparatus side by side so arranged that when the oxygen or air is turned from one it goes on to the

other, and six potash bulbs, can make 48 combustions per day of nine hours.

After each day's work it is necessary to wash the sand in the tube by running a stream of water through it; remove any moist calcium chloride from the tube next the cooler and replace it with fresh or, better still, put in an entirely new tube full of freshly dehydrated calcium chloride and dry the moist one to have it ready for use the day following. The worm also should be dried out about every two days by placing it over a burner and blowing air through it.

In our practice we have found that about 25 combustions can be made on each bulb before it will need refilling with calcium chloride and caustic potash solution. If more than this number be run on a bulb it will be found that the calcium chloride has ceased to catch all the moisture carried from the potash solution. The latter has a specific gravity of 1.27 and is capable of absorbing 2.5 grams of carbon dioxide with perfect safety.

I append some of the results obtained by the above method of combustion and by combustion in a platinum tube.

Sample. No	Combustions in a platinum tube. Per cent. carbon.	Combustions in a porcelain tube by new method. Per cent. carbon.
16	0.836	0.832
17	0.850	0.860
17	....	0.864
17	....	0.864
1238 B C 389	0.563	0.566
1238 B C 389	....	0.552
1580	1.111	1.108
1099 C	1.087	1.075
1099 C	1.073	....
1078 C 291	1.162	1.168
1078 C 291	....	1.164
1060 C 283	0.326	0.323
R. J.	0.958	0.958
R. J.	0.955	0.953
R. J.	0.953	0.955
J.	1.067	1.068[1]
J.	1.070	....
B	0.904	0.900[1]

[1] These results were obtained when exhibiting the apparatus before the Philadelphia Section of the American Chemical Society; the carbon content of the steel was unknown to me at that time. The results obtained by combustion in a platinum tube are those of R. Job, chemist of the Philadelphia and Reading Railway Co., also of A. A. Blair.

Some duplicate results obtained by combustion in a porcelain tube by the new method are:

Sample No.	Carbon Per cent.
1	0.839
1	0.839
5	0.838
5	0.832
8	0.776
8	0.779
9	0.850
9	0.855
11	0.843
11	0.842
14	0.848
14	0.853
713	1.012
713	1.019
B X	1.608
B X	1.614

The condenser or worm cools the gases so that when they reach the weighed potash bulb, there is no tendency to carry out moisture while running the bubbles at the speed of five per second. In fact, blanks have shown that the gases can pass through the potash bulb at a speed so great that the bubbles are scarcely to be distinguished and no loss in weight will be sustained.

	Gain or loss in weight of bulb.	Number of bubbles per second.
Blank	0.0000	5
"	0.0000	5+
"	+0.0003	steady stream

Two weighed potash bulbs placed one after the other and a combustion of a high carbon steel made with the oxygen running five bubbles per second and the air a trifle faster, gave the following:

Sample. No.		Before. Grams.	After. Grams.	Difference. Grams.
1905 B X 347	Weight of 1st bulb	17.4991	17.5920	0.0929
1905 B H 347	" of 2nd "	23.0177	23.01755	0.00015

A factor weight, 2.7272 grams, of the drillings was taken.

The porcelain tube may be replaced with a copper tube 16 inches long, $\frac{5}{8}$ inch in diameter, and $\frac{1}{16}$ inch walls, water-jacketed at each end for $1\frac{1}{2}$ inches, as these results show:

Sample.	Combustion in a porcelain tube. Per cent. carbon.	Combustion in a copper tube. Per cent. carbon.
Standard No. 1	0.529	0.529
" " 1	0.529[1]	0.527
" " 2	0.544	0.545

The copper tube, however, burns out in about two weeks, while the porcelain tube, with proper care, will last for weeks, especially if at the heated portion, the boat be kept from direct contact with the tube by a sheet of platinum foil.[1]

The life of the copper oxide tube is about three months. When it is burned out, however, it is quickly replaced, by another, the water-jackets being easily melted from the old tube and soldered on the new.

The whole apparatus can be made in any laboratory at a very small cost.

Mr. Job, who now has this apparatus in use in the laboratory of the Philadelphia and Reading Railway Co., has obtained very good results, a few of which he kindly gave me.

	Combustion in porcelain tube.	
	Old method. Per cent. carbon.	New method. Per cent. carbon.
Standard No. 1	1.070	1.068
" " 3	0.937	0.937–0.942
" " 2	0.527	0.531
Blank	....	0.0000
"	....	0.0000

It may be stated that in almost every instance where blanks have been made, the difference in weight of the potash bulb has been zero. This is due, I believe, to the cooler, which permits the gases to pass into the potash bulb at the same temperature, or a slightly lower one, at which it leaves it; consequently the gas is saturated with moisture to the same degree. For this reason, I believe the accuracy of the determinations even exceeds the results obtained by the old method where a dry train is used.

Many of the results that have been given, that is, those coming from this laboratory, have been made in the course of our everyday work by a man turning out a result every ten minutes from two of these pieces of apparatus, and they certainly show that,

[1] Old method combustion in platinum tube.

[2] Since the foregoing was written, Mr. Job has informed me that he has obtained excellent results by using a hard glass tube protected from the flames by a piece of iron, and supporting the boat within the tube in a sheet of platinum foil.

even at this rapid rate, the accuracy attained equals that of the more slow and painstaking method of combustion in a platinum tube.

It may be of interest to know that the copper oxide may be replaced by the electric spark as an oxidant to insure the complete change of the carbon to carbon dioxide. The action of the electric spark on a mixture of carbon monoxide and air, in the presence of moisture, is to produce carbon dioxide, ozone, and a very small amount of nitric acid; therefore, I removed the copper oxide from the system and placed in its stead a small glass tube through which two platinum wires were fused so that a spark would be produced between the points when a current from a Rhumkorff coil passed through the wires. Combustions were then made as usual, except that during the time of burning in oxygen, a continuous stream of sparks played between the platinum wires within the tube. The following table shows the results obtained:

Sample. No.	Method.	Weight of carbon dioxide. Grams.	Carbon. Per cent.
1.30 Standard	Electric spark as oxidant	0.1303	1.303
1257 B D	" " " "	0.0720	0.720
1257 B D	No oxidant	0.0614	0.614
1257 B D	CuO as oxidant—combustion in platinum tube	0.0724	0.724
1254 B D	ditto	0.0747	0.747
1254 B D	Electric spark as oxidant	0.0744	0.744
Pig iron	" " " "	0.4193	4.193
Pig iron	CuO as oxidant—combustion in platinum tube	0.2060	4.120*

Starch paper moistened with potassium iodide and placed just before the weighed absorption bulb was turned blue, showing the presence of ozone.

Owing to the platinum contacts of the induction coil becoming worn away with continued use and the consequent stoppage of the sparks, thus creating error, the hot copper oxide is preferred as an oxidant. Could, however, the trouble with the induction coil be simply remedied, the apparatus without the copper oxide would be the neatest, cleanest, and most compact to use.

Mr. John K. Faust has made most of the determinations in-

*In every case except that marked with an asterisk, where a half factor weight was taken, a whole factor weight, 2.7272 grams, was taken.

volved in perfecting this method of carbon combustions, and its success is largely due to his careful work, for which I sincerely thank him. I also wish to thank Mr. F. Cooper Pullman for his assistance in working up the electric spark as an oxidant.

LABORATORY OF THE CARPENTER STEEL CO., READING, PA.

SOIL HUMUS. SOME SOURCES OF ERROR IN ANALYTICAL METHODS.

BY A. L. EMERY.

Received April 21, 1900.

DURING the past four years we have devoted considerable time in our laboratory to the analysis of California and Hawaiian soils for the purpose of determining the kind of fertilizer best adapted for each separate piece or tract of land. The analytical methods of Dr. E. W. Hilgard have been generally followed in our work and good results have been secured with the exception of the determination of humus and nitrogen in the humus. In order for a method to be practical for industrial work it must be rapid as well as accurate. Time is a very important factor. Many samples of soils require several days' leaching to free them of calcium salts and several days more for the extraction of the humus.

About two years ago while working with one of these slowly leaching soils it was observed that the caustic potash solution of humus was strongly ammoniacal. A slightly ammoniacal solution is, of course, unavoidable, for caustic alkalies will liberate the ammonia present in the form of ammonium salts and also readily decompose some of the weaker compounds of amid nitrogen. But where the time of leaching extended over several days more ammonia was apparently liberated, than was originally present in the form of these easily decomposed salts. Other work prevented further investigation at that time, and the subject was not taken up again until this winter when the rush of soil samples to the laboratory almost compelled experimenting with humus with a view of finding a more rapid method. During these experiments some interesting results developed.

Several samples of soil, washed free of calcium salts with dilute hydrochloric acid, were leached with a 4 per cent. solution of caustic potash. In the course of a few hours, varying with the

richness of the sample in nitrogen, a piece of red litmus suspended in the mouth of the flask containing the leached solution would turn blue in ten or fifteen minutes. The same solutions, after standing twenty-four hours, would liberate enough ammonia to turn the litmus blue in about five minutes, and after standing several days the change of color was very quick. In several cases the ammonia could even be detected with the nose. From 5 to 10 grams of soil were used for leaching.

The above being true, it follows that the determination of nitrogen in the caustic potash extract is always too low by the amount of nitrogen lost in the form of ammonia. This loss apparently depends on the nature of the soil sample, the time occupied in leaching, and the care taken to prevent the ammonia escaping from the leaching apparatus. Therefore, since the nitrogen in the caustic potash extract is too low, it follows that the nitrogen in the humus would also be too low. This loss of ammonia doubtless partly explains the great liability of duplicate results of the determination of nitrogen in humus to disagree, and more particularly accounts for the variation in results by different analysts.

By Dr. Hilgard's method[1] humus is determined by evaporating the solution, leached from calcium-free soil with dilute ammonia, drying to constant weight, igniting, and weighing. The difference in weight is regarded as humus.

During the process of evaporation the ammoniacal humus solution undergoes digestion at the temperature of the water- or steam-bath. Either during this digestion or during the leaching process (probably during both), ammonia is absorbed from the leaching solution and enters into stable combination with the humus extract. The free ammonia is easily expelled by evaporation, but the humus residue left in the platinum dish after being dried at 100°, or even 110° C., retains part of the ammonia at least that it has taken into combination from the leaching solution. This added ammonia is easily expelled with lime or magnesia, but not all the nitrogen of the residue is thus driven off even with dilute caustic potash. The following analyses will illustrate this point:

[1] Wiley's "Agricultural Analysis," Vol. I, p. 324, § 311.

Total nitrogen in soil by direct determination. Gunning method.[1]	Humus.	Nitrogen in humus extracted with caustic potash.	Nitrogen in humus extracted with NH_3, evaporated and dried at 100° C.
Per cent.	Per cent.	Per cent.	Per cent.
0.159	1.860	0.67	0.97
0.097	0.775	4.39	9.39

It was at first thought that the difference in the per cent. of nitrogen in the caustic potash extract and the ammonia extract represented the loss of nitrogen in the form of ammonia during the extraction with caustic potash, but it was found that a similar difference existed when the utmost care was exercised to prevent the escape of ammonia from the caustic potash solution, both during and after leaching.

These results led to the analysis of the soil residues which had been leached with caustic potash and those which had been leached with ammonia. *Approximately 50 per cent. of the total nitrogen originally present remained in the soil after leaching with caustic potash.*

Total nitrogen in soil.	Nitrogen left in soil after leaching with caustic potash.
Per cent.	Per cent.
0.159	0.097
0.132	0.066
0.097	0.038

The average of the second column of figures is very close to 50 per cent. of the first, or the total nitrogen in the soils. Present data is insufficient to determine whether this ratio is true for soils taken from all parts of the state. The above samples and others showing similar agreement are mostly from the Santa Clara valley.

After leaching with ammonia and drying the soil residue at 100°C. or distilling the residue until the distillate was neutral to litmus paper, from a little over $\frac{1}{2}$ to $1\frac{1}{2}$ the amount of total nitrogen originally present in the soil was found in the residue. Results seemed to vary somewhat with the time occupied in expelling the free ammonia from the soil residue by heat, the

[1] Ten grams of soil may be readily digested by this method.

distillation method giving slightly higher results than by drying at 100° C. This might have been expected since the conditions of the two processes are not exactly the same. One sample of Hawaiian soil containing 0.812 per cent. total nitrogen took up 0.430 per cent. of nitrogen from a 2 per cent. ammonia solution by digestion at the room temperature over night and retained it at 100° C. This gave a total nitrogen of 1.242 per cent.

These results seem to strongly indicate that the organic or mineral constituents of the soil left on the filter have the power to absorb ammonia from the leaching solution during the process of leaching to a far greater extent than has heretofore been supposed. It seemed highly probable that the soluble organic compounds in the extract, called humus extract, would also have this power of taking ammonia from the leaching solution. This point was demonstrated in the following manner: Five grams of soil, washed free of calcium salts, were distilled with lime and the nitrogen in the distillate determined. Then five grams of the same soil were extracted with ammonia after removing the calcium and magnesium salts according to Dr. Hilgard's method. The free ammonia was expelled from the extract by evaporating to dryness and the resulting residue distilled with lime and the nitrogen determined in the distillate. This was repeated with a number of samples and while the results seemed to vary considerably yet more nitrogen was invariably obtained from the ammonia extract distilled with lime, than from the soil distilled with lime. In the first case, that is where the soil was distilled with lime, it will be noted that the organic compounds which are insoluble in dilute caustic alkalies as well as the soluble ones were subjected to the action of lime in hot solution. Since lime will decompose some of these insoluble nitrogenous compounds it follows that more nitrogen should have been obtained in the first case than in the second had not the soluble organic compounds, leached from the soil, taken up nitrogen in the form of ammonia from the ammoniacal leaching solution. Hence, we conclude that Dr. Hilgard's method gives too high results for humus by the amount of ammonia taken up from the leaching solution and held in combination by the extracted organic matter.

Now, since nitrogen in the humus is determined by dividing the nitrogen in the caustic potash extract, which is too low, by

the humus, which is too high, the error would be multiplied and the result would be invariably too low. That this error is quite large and not to be neglected is clearly shown by the figures given above.

By a slight modification of the method the ammonia can be prevented from escaping during leaching with caustic potash. The following method seems to overcome all difficulties : The soil to be leached with caustic potash is placed in a funnel which is closed at the top with a stopper through which the leaching solution is admitted by a separatory funnel. The glass support of a Gooch crucible serves very well for the funnel holding the soil. The solution from the soil is run directly into dilute sulphuric acid, the bottle containing the same being sealed with a U-tube containing sulphuric acid. Gentle suction can be applied to this apparatus which greatly hastens the process without the least danger of losing ammonia.

It is more difficult to correct the second source of error; *i. e.*, the absorption of ammonia by the organic matter extracted from the soil. No very satisfactory results have been obtained although considerable time has been devoted to the matter.

Before leaching the soil for the extraction of the humus, it is washed with dilute hydrochloric acid until the filtrate shows no reaction for calcium. It is well known that the organic acids of soils form single and double salts with the alkali earths and with the oxides of some metals. Calcium is a stronger base than ammonia ; therefore, an acid that would liberate calcium ought also to liberate ammonia from these double insoluble salts. We had supposed that this hydrochloric acid solution contained practically only the nitrates and nitrites present in the soil which would be worth considering only in exceptional cases.

Total nitrogen in soil.	Total nitrogen leached out with hydrochloric acid.	Nitrogen leached out with hydrochloric acid which is liberated with lime.
Per cent.	Per cent.	Per cent.
0.159	0.037	0.011
0.812	0.049	0.036

The above results show that it is not safe to assume the insol-

ubility of organic matter and organic salts even in very dilute hydrochloric acid. We believe this also may be a source of no insignificant error in soil analysis.

It would be interesting to know whether the organic matter of soils of humid regions show the same tendency to absorb ammonia in such relatively large amounts as the soils that we have examined. This absorption of ammonia seems to take place at ordinary temperature as well as in hot solutions. The rate or maximum amount of absorption has not yet been determined. Hitherto we have regarded free ammonia as being occluded in the soil but it now seems highly probable that one of the functions of the organic matter of the soil is to absorb the free ammonia which comes to it in solution and that which is liberated in the soil itself. Possibly in nature occlusion precedes and directly aids absorption and combination.

Regarding the nature of humus little seems to be really known. If humus is regarded as the organic matter and mineral salts of organic acids extracted from soils by means of dilute alkalies we have to deal undoubtedly with a highly complicated mixture of chemical substances in various stages of decomposition and combination. Many organic nitrogenous substances are soluble in dilute alkalies without having undergone a process of decomposition. This is true of the organic matter of plants as well as that of animals. Sun-dried grass, weeds, or wood, according to the generally accepted idea of the term, would not be regarded as humus. Yet, 27.30 per cent. of a sample of clover meal dissolved in 25 cc. of a 5 per cent. solution of ammonia at room temperature by standing over night. The undissolved portion contained 2.94 per cent. nitrogen. Providing this residue took up no free ammonia from the solution, which is doubtful, 35.76 per cent. of the total nitrogen of the clover meal was readily soluble and probably more would have been dissolved had the leaching process been used.

This is more or less true of other organic substances which find their way into soils and form a part of them. While clover meal may be an excellent fertilizer much of it would, nevertheless, have to be regarded as humus by the present methods of analysis. In fact in many respects clover meal extract acts as

humus is supposed to act. Part of it forms insoluble salts with calcium and is precipitated with alcohol.

If a soil be boiled with an excess of calcium or barium salts and the soil afterwards extracted with ammonia the filtrate will usually have a color closely matching that of dilute ferric chloride. If the same soil is then leached with hydrochloric acid and again leached with ammonia, the resulting solution will have a much darker color which is often almost black. Yet barium or calcium salts precipitate the organic matter in the caustic potash soil extract, leaving an almost colorless supernatant liquid. The precipitation is not quantitative.

Further experiments are already under way in the laboratory and we hope to have further data of interest in regard to humus and soil analyses in connection with field experiments with fertilizers.

CHEMICAL LABORATORY OF N. OHLANDT & CO.,
April 2, 1900.

LECTURE EXPERIMENTS. REVERSIBLE CHEMICAL REACTIONS.

BY W. LASH MILLER AND F. B. KENRICK.

Received April 11, 1900.

LECTURES on physical chemistry are, at present, less in need of experimental illustration than those on any other branch of the science, being delivered, for the most part, to small classes of advanced students, who have ample opportunity for experimenting in the laboratory. Some of the conceptions and discoveries which form the subject-matter of that department have, however, proved of such importance, that it is very desirable to incorporate them into the elementary course. This has hitherto been rendered difficult by the lack of suitable lecture experiments.

Among the most important of these discoveries, is that of the *incompleteness* and *reversibility* of a very large number of chemical reactions. The application of thermodynamical methods in the treatment of such cases is an achievement of the present day, and necessarily forms one of the chief subjects of study of advanced classes. The "average student," however, whose practical acquaintance with chemistry is limited to a course in

analysis, knows nothing of all this. He knows the chemical reaction as a quantitative, non-reversible, and practically instantaneous phenomenon.

It does not occur to him that the reactions he meets with in the laboratory have all been selected because of these very properties, which render them convenient for the purposes of the analyst; generalizing from his one-sided experience, he is apt, half unconsciously, to form views on chemical affinity practically identical with those of Bergmann. Theories based on the rate of inversion of cane-sugar, and on Berthelot's experiments with alcohol and acetic acid—the experiments themselves are, unfortunately, quite unsuited to the lecture table—do not make much impression on one whose daily experience points in the other direction; if anything, they serve only to accentuate the feeling of unreality associated with the "other world" of organic chemistry.

Reactions involving the addition and removal of water of crystallization, or the formation and decomposition of double salts or other "molecular" compounds are likewise unsatisfactory. To be convinced, the student must see a "genuine" chemical reaction, *i. e.*, one used in analysis or on the large scale in chemical manufacture, reversed before his eyes.

The following half dozen reactions have been selected from this point of view; the instructions include all the details that we have found necessary in exhibiting them before a large audience.

I. AMMONIUM THIOCYANATE AND FERRIC CHLORIDE.

Approximately equivalent solutions of these substances are prepared, the first containing:

Ammonium thiocyanate	7.5 grams
Water	to make 200 cc.

and the second:

Commercial (basic) ferric chloride	6 grams
Concentrated hydrochloric acid (sp. gr. 1.175)	25 cc.
Water	to make 200 cc.

Five cc. of each are mixed in a large beaker, about two liters of (tap) water added, and the orange-colored mixture poured in equal quantities into four beakers.

To the	is added	The color becomes	Reaction.
first	5 cc. am. thiocyanate solution.	dark red	⟶
second	5 cc. ferric chloride solution.	dark red	⟶
third	50 cc. saturated am. chlor. sol.	almost colorless	⟵
While the fourth is kept for comparison.		orange	

If the reaction be represented by the equation

$$FeCl_3 + 3NH_4SCN \rightleftarrows Fe(SCN)_3 + 3NH_4Cl$$

and the amount of ferric thiocyanate be judged from the depth of color of the solution, the reaction between equivalent quantities must be regarded as incomplete. The changes of color are interpreted by the arrows in the last column (indicating the direction of the reaction).

In order to show the effect of dilution in destroying the ferric thiocyanate (dissociation), equal quantities of the orange-colored mixture may be placed in two rectangular glass troughs of equal width, one of which is about twice as thick (from back to front) as the other. Water is then added to the solution in the larger trough until the level is the same in both, and a piece of white paper held at a little distance behind the two troughs. Seen from the front, the more dilute solution appears much less deeply colored than the other. For purposes of comparison, indigo or potassium permanganate may be used, which give the same color in the two vessels. Rectangular battery jars answer very well, as the change in color is so marked that unevenness in the glass is of no moment.

II. BISMUTH CHLORIDE AND WATER.

A "bismuth solution" is prepared as follows:

Commercial "bismuth trisnit" ..... 40 grams
Hydrochloric acid (sp. gr. 1.175) ..... 40 cc.

Rub together in a mortar, as the powder cakes; a trifling residue may be filtered off.

The reaction with water is represented by the equation:

$$BiCl_3 + H_2O \rightleftarrows BiOCl + 2HCl.$$

To 50 cc. water add 5 cc. bismuth solution ..... ⟶
Add 5 cc. hydrochloric acid (sp. gr. 1.175) ..... ⟵
" 75 " water ..... ⟶
" 5 " acid ..... ⟵
" 200 " water ..... ⟶
" 10 " acid ..... ⟵
" 500 " water ..... ⟶
Pour in acid from the reagent bottle ..... ⟵

The reaction may be carried out in a glass cylinder, about three inches in diameter, holding about a liter. If small marks be made at the proper heights on the cylinder the water may be poured in without measuring.

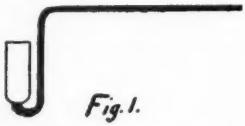


Fig. 1.

The acid may be delivered from a pipette or burette, or it may be dipped out of a beaker with the little measure figured in the margin (made of a piece of test-tube and a glass rod).

III. AMMONIA WITH SALTS OF COPPER AND OF SILVER.

Silver Bromide.—Excess of potassium bromide is added to 15 cc. of fifth-normal silver nitrate solution; the precipitate is washed once by decantation, shaken with 15 cc. of ammonia (sp. gr. 0.915) and filtered. In the solution so obtained a precipitate is produced,

(*a*) adding a drop of potassium bromide solution,
(*b*) adding a drop of silver nitrate solution,
(*c*) adding five times its volume of water,
(*d*) boiling, or
(*e*) exposing (in a fractionating flask) to the vacuum of a filter-pump.

Copper Sulphate.—Five cc. copper sulphate solution (100 grams blue vitriol in 1 liter) are mixed with 5 cc. 5/1 normal ammonia and diluted with 400 cc. *distilled* water. The addition of 400 cc. more distilled water produces a precipitate. If the reaction be carried out in a flat glass cell (an inch thick) with an incandescent lamp behind it, the change from clear to turbid is very distinct. This experiment should be rehearsed immediately before the lecture, as the presence of traces of acid, carbon dioxide, or ammonia salts, largely increases the amount of water necessary to produce a precipitate. If tap water be used instead of distilled water, half as much again may be required.

IV. FORMATION AND DISSOCIATION OF WATER, ETC.

Eudiometer.—A very convenient lecture table eudiometer con-

sists of a straight glass tube (10 mm. diameter and 760 mm. long) open at one end and fused to a capillary with capillary tap at the other. The platinum wires are sealed through the wide tube just below its junction with the capillary, and the divisions are marked with rings of Brunswick black. A piece of iron pipe, widened at the mouth, serves as a mercury trough.

Fig. 2.

Measured volumes of the various gases (H_2, O_2, CO, Cl_2, etc.) may be admitted through the tap, if the eudiometer be first filled with mercury, and the division corresponding to the volume desired be set level with the surface of the mercury in the iron tube.

The union of two volumes of carbon monoxide with one of oxygen may be shown by introducing a little 30 per cent. potash above the mercury in the eudiometer; while in a subsequent experiment (without potash) the volume of the carbon dioxide formed may be determined.

The formation of hydrochloric acid from one volume of hydrogen and one of chlorine may be shown with a fair degree of accuracy, if the mercury trough be replaced by brine from the chlorine gasometer in a tall glass cylinder.

In many cases, notably with CO and O_2, the gases must be mixed by shaking the tube vertically before passing the spark, or no explosion will occur.

Deville's Tube (Fig. 3.).—A coil of platinum wire hung vertically in the neck of a fractionating flask and heated by electricity, is just as efficient as any other "white hot platinum tube" in bringing about the dissociation of water vapor. It works very much better than the noisy induction sparks commonly employed.

If concentrated ammonia (sp. gr. 0.880) be warmed in the flask, the apparatus may be made use of to effect the decomposition of NH_3 into N_2 and H_2.

V. SULPHURIC ACID AND SODIUM CHLORIDE.

1. Concentrated sulphuric acid is poured into its own volume

of a saturated solution of common salt in a test-tube. The mixture may be cooled under the tap and shaken; but in general a

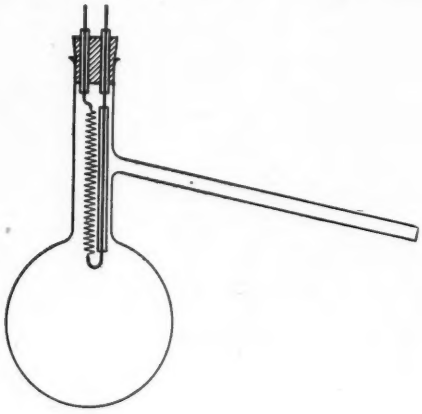


Fig. 3.

crystal of Glauber's salt must be added before crystallization will occur. The liquid is poured off, and the crystals dried on a piece of unglazed porcelain.

2. If some of the sodium sulphate so prepared be covered with concentrated hydrochloric acid (on a watch-glass) it is at once changed to a fine powder of sodium chloride; which, in turn, may be freed from acid on a porous plate.

To demonstrate the change from chloride to sulphate, and back again, mix a drop of the original salt solution with a little water on a piece of glass the size of an ordinary lantern slide; warm till crystallization sets in, and throw the image on the screen (Fig. 4). The same may be done with small portions of the sulphate (Fig. 5) and sodium chloride formed in the experiment.

VI. ANTIMONY CHLORIDE AND HYDROGEN SULPHIDE.

An antimony solution is prepared as follows: Dissolve 2 grams tartar emetic in 15 cc. hydrochloric acid (sp. gr. 1.175); then

add 85 cc. water. (This solution cannot be kept more than two or three hours as a precipitate of oxychloride is slowly formed.)

$$2SbCl_3 + 3H_2S \rightleftarrows Sb_2S_3 + 6HCl.$$

(*a*) Pass a little H_2S into 5 cc. antimony solution ..... ⟶
(*b*) Add 8 cc. hydrochloric acid (sp. gr. 1.175) ..... ⟵
(*c*) " 5 " antimony solution ..... ⟶
(*d*) Heat, not to boiling ..... ⟵
(*e*) Cool again (in a dish of water) ..... ⟶
(*f*) Add 6 cc. hydrochloric acid ..... ⟵
(*g*) Pass in H_2S under pressure of 3 meters Hg ..... ⟶
(*h*) Reduce pressure by filter-pump ..... ⟵

Notes.—(*c*) If the addition of antimony does not bring down

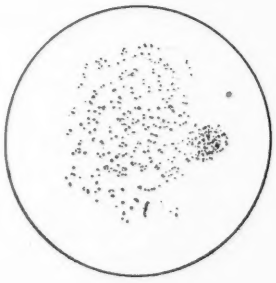


Fig. 4.

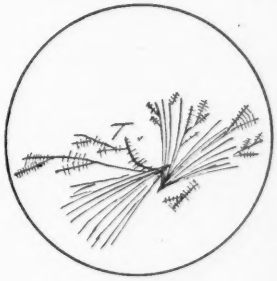


Fig. 5.

a fairly heavy precipitate, hydrogen sulphide should be passed in again, or there will be no precipitate in (*e*).

(*e*) Cool only until a precipitate appears, then add the acid (*f*) and finish cooling; if too much precipitate is formed it dissolves very slowly in the acid.

(*g*) The necessary pressure may be secured by means of the pump described below. With a rubber "syringe" (bulb and two valves) worked by hand, a pressure of about one meter of mercury (above the atmosphere) may be maintained; this is sufficient for the purposes of the experiment, but the precipitate comes much more slowly than when the pump is used. The object of the vacuum (*h*) also is to save time.

The reaction may be conveniently carried out in the glass ves-

sel represented in Fig. 6. The hydrogen sulphide enters by *A* which may be tied in by wire round the ears *E*. *A* is connected to the pump by rubber pressure tubing, and *B* (the outlet) to

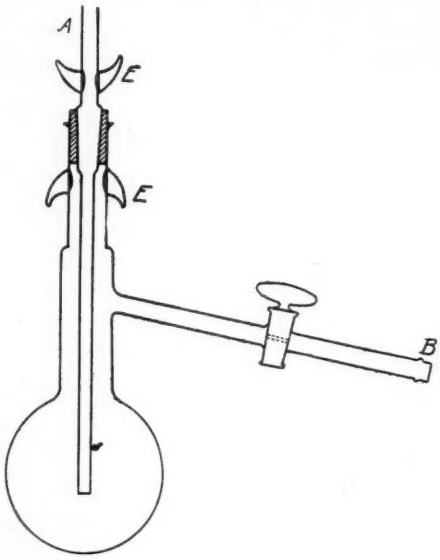


Fig. 6.

the flue. All taps should be wired in. Joints may be made with ordinary rubber tubing covered with cloth and wired.

VII. PRESSURE PUMP FOR GASES.

The accompanying figure (Fig. 7[1]) represents the pump referred to in the preceding paragraphs. It consists of three pieces of black rubber tubing T (of which two are shown in the figure) each 1 inch in diameter and 18 inches long, closed at the bottom and connected at the top by glass tubing to a pair of Bunsen valves. The valves are shown separately in Fig. 8 and are so arranged that on compressing the tubes the gas contained in

[1] For the sake of clearness, the taps and handle which are actually *behind* the cylinder, are represented *to one side* of it.

them is forced out through D, and on removing the pressure they are refilled through F.

The compression is effected by moving the handle *H* to the position indicated in the figure, thereby opening the brass tap *W* (communicating with the water mains) and closing *S* (to the sink). Water thereupon flows through the glass pipe *P* into the

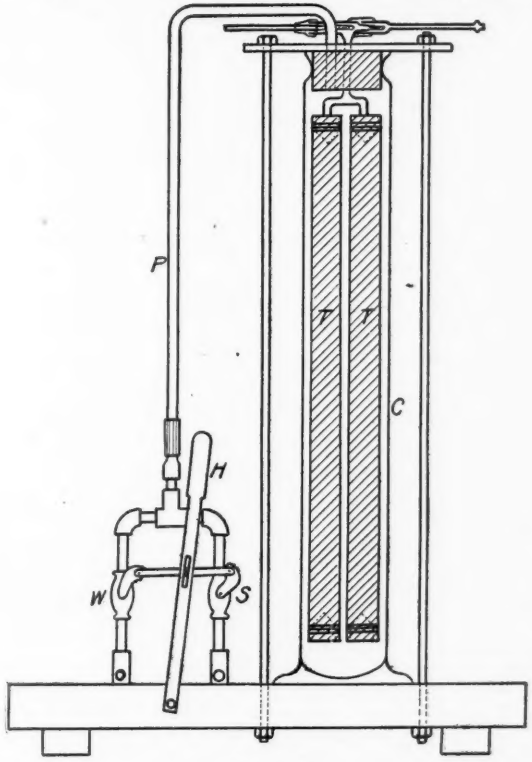


Fig. P.

glass cylinder *C* containing the rubber tubes *T*. Moving the handle in the opposite direction fills the tubes again with gas.

The top of the cylinder is closed by a rubber plug covered with a brass plate ($\frac{1}{4}$ inch thick) which is held down by four $\frac{1}{4}$-inch

brass rods threaded at the ends and provided with nuts. The ends of the tubes are closed by glass plugs, wired in; in order to keep the rubber from tearing, a wedge-shaped piece of cork is inserted at each end, as shown by the dotted lines in the figure.

The capacity of the pump is 500 cc. Three strokes are sufficient to attain the maximum pressure in the antimony sulphide experiment.

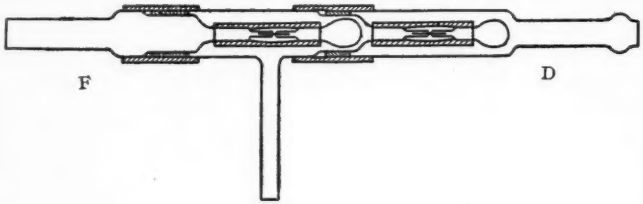


Fig. 8.

With this apparatus a gas can be brought to the pressure of the water system *without coming into contact with any liquid.* Higher pressure may be attained by using a force pump; the limit depends only on the strength of the apparatus and on the ratio between the variable volume (rubber tubing) and the constant volume (glass tubing) between the valves.

THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TORONTO, April, 1900.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 23.]

A NEW ELECTROLYTIC CELL FOR RECTIFYING ALTERNATING CURRENTS.

BY W. L. HILDBURGH.

Received April 3, 1900.

IN electrical work an automatic device which will permit a current to pass through it in one direction only is frequently desirable, for rectifying alternating currents, for example, or for preventing a back-flow of current due to polarization. In addition to mechanical commutators several arrangements for the purpose have been previously known, but, with one exception, they are applicable to comparatively high voltages only. This exception is the two-cell rectifier described by Prof. M. I. Pupin

before the American Physical Society.[1] In the present paper a new class of electrolytic cells capable of affecting currents of extremely low voltage is described. These cells act by the production of a counter E. M. F. of polarization whose intensity depends on the direction of the E. M. F. impressed, and have been termed "Single Cell Rectifiers."

If a plate of copper be placed in dilute sulphuric acid it will not dissolve. If, however, a platinum electrode be placed in the acid, and the copper made the anode, a very small E. M. F. is sufficient to cause the copper to dissolve freely and hydrogen to be deposited on the platinum, and a current will pass until all the copper is carried into solution. When the source of the E. M. F. is reversed a momentary current passes, the platinum plate becomes covered with oxygen, and, if the impressed voltage is not too high, the current ceases almost completely. That is, the cell Cu | H_2SO_4 | Pt, producing no current, permits the passage of continuous currents of low E. M. F. through it in one direction only.

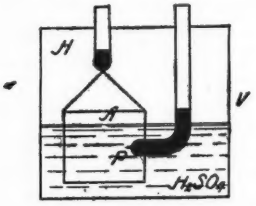
By placing a number of such cells in series it is possible to prevent the flow of a current of any voltage whatsoever. Such a cell may be used for the rectification of alternating currents by so regulating the size of the platinum plate that the quantity of current necessary to polarize it as anode is less than that which passes during the next half-wave, when the platinum acts as cathode. The smaller the platinum, or passive plate, the higher the degree of rectification (asymmetrical efficiency) attainable. The amount of rectification is dependent, however, not only on the size of the passive plate, but also on the quantity of current which can pass; that is, on the *current density* at the surface of that plate. Consequently the lower the resistance in the circuit or the lower the frequency of the alternating E. M. F. impressed the greater will be the asymmetrical efficiency.

In the cell Cu | H_2SO_4 | Pt, or more properly speaking, Cu | $CuSO_4$ | H_2SO_4 | Pt, considerably more energy is required to produce hydrogen at the passive plate than is given out by the solution of the copper, or active plate. As this evidently lowers the efficiency of the device by producing an E. M. F.

[1] June, 1899.

counter to the main flow of current, means should be adopted of making the energy given out at the active plate and that absorbed at the passive as nearly equal as possible. By making the active plate of the substance given off at the passive plate by the current in the "useful" direction this condition can be nearly fulfilled. The substance produced at the passive plate should be a gas, as otherwise that electrode will soon become covered with a layer of active substance and cease to be inert. Gaseous active electrodes may be formed with hydrogen, oxygen, chlorine, etc., as the active material, absorbed by platinum or in chemical combination with some metal.

Of such electrodes the writer has found that hydrogen when absorbed by platinum black gives by far the best results, and can be made, in addition, self-regenerating, giving a "continuous-acting" rectifier such as is shown in illustration. V is a sealed vessel into which pass two mercury-contact electrodes A and P. A, the active plate, is of platinized platinum, partly in hydrogen



gas (H) and partly in sulphuric acid (H_2SO_4). P, the passive electrode, is a platinum wire sealed into glass and cut off to give the desired surface of contact with the liquid, or filed plane with the sealed end of the tube. The "useless" current carries oxygen to P, but is of insufficient voltage to produce bubbles, and the cell polarizes. In the opposite, or "useful" direction hydrogen is carried from A to P, is there given off in bubbles, and goes back to join again the gas H. It is clear that since nothing but hydrogen is produced at P, provided the impressed E. M. F. is not too high, that the cell will work for an indefinite time, or until changes in the surface of the platinum electrodes stop the actions described.

For the most perfect action of rectifiers of this class there

should be no counter E. M. F. in the "useful" direction. In the hydrogen-cell it requires from a few thousandths of a volt to 0.085 volt to carry the gas through the electrolyte, the pressure varying with the size of the passive electrode and the condition of its surface, the concentration of the liquid, the temperature, etc. This counter E. M. F. can be "balanced," as is necessary for certain kinds of work, by adding an E. M. F. in the "useful" direction, taken from a slide-wire in series with 1 or 2 cells of battery.

It is impossible to specify the size of the various parts of a cell without knowing all the conditions under which it is to be used. As a general rule the small (passive) electrode should be of the dimensions of a millimeter, ranging in area from a small fraction of 1 sq. mm. up to 100 sq. mm., according to the frequency and the resistance or inductance in the external circuit. The platinized electrode should be of sufficient size to absorb hydrogen as fast as it is given off at the passive plate. For the electrolyte 1 part sulphuric acid to about 8 or 10 of distilled water, from which the oxygen has been removed by boiling or exhaustion, serves very well. The vessel need only be large enough to contain the two electrodes and a little liquid and gas, the latter two being employed continuously, and only a very small quantity being in use at any one time. The larger electrode should be thoroughly washed after platinizing, as otherwise platinum may be carried to the smaller electrode, impairing the efficiency. A jar of water, in which the cell may be kept, offers a convenient method of sealing, for laboratory use.

The following points will be found of service in working with the cell, and have been obtained, for the most part, by the study of curves taken with alternating currents. More complete expositions of the theory and actions of rectifiers of this class will be found in other papers by the writer.[1]

The smaller the plates the greater the asymmetrical efficiency.

The greater the resistance in the circuit the less the asymmetrical efficiency.

The higher the frequency the less the asymmetrical efficiency.

The higher the frequency, or the greater the resistance, or the larger the plates, the higher may be the impressed alternating

[1] *Elec. World and Eng.*, 1900; *School of Mines Quarterly*, July and Oct., 1900.

E. M. F. in a given cell, without producing oxygen bubbles at the smaller plates.

In a perfectly "balanced" rectifier, as long as the impressed E. M. F. is not too high, the quantity of current capable of doing unidirectional work is proportional to the impressed E. M. F.

If the active E. M. F. of a rectifier be too high a continuous current will flow, and the amount of rectification be dependent on the impressed E. M. F.; if the latter below, rectification may cease completely.

If the active E. M. F. be too low the amount of rectification is dependent on the impressed E. M. F., and may become zero if the latter be low. This property prevents the use of rectifiers in circuits in which any considerable counter E. M. F. is produced.

Rectifiers for high E. M. F. can be formed by joining a number of cells in series. The passive plates in each can then be correspondingly increased in size, while the whole set gives the same efficiency as one of the cells gave before its electrode was enlarged. The number of rectifiers and the impressed E. M. F. should be proportioned to their circuit exactly as primary cells are proportioned, each primary cell being represented by a rectifier and a certain portion of the impressed E. M. F.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 24.]

A METHOD FOR THE DETERMINATION OF ELECTRICAL CONDUCTIVITY WITH DIRECT CURRENT INSTRUMENTS.

BY J. LIVINGSTON R. MORGAN AND W. L. HILDBURGH.

Received April 3, 1900.

IN the determination of electrical conductivity, in order to prevent errors, it is necessary to use an alternating current whose frequency is of such a value that the electrodes, during a half period of the alternating current, receive a polarization which is negligible compared to the voltage impressed. Up to the present time it has been difficult to detect small quantities of an alternating current, except by aid of the telephone. In the

Kohlrausch-Ostwald method the electrolyte is placed in one arm of a Wheatstone bridge, an alternating current passed through it and the resistance balanced on the bridge wire against a known value by aid of the telephone. McIlhiney[1] passes a direct current through a direct current measuring instrument and then transforms it into an alternating current with a rotating pole changer and carries it through the electrolyte.

One of us[2] has designed a number of rectifying cells for the purpose of permitting the passage of current in one direction only, so that an alternating current in going through them is more or less rectified and has many of the properties of a direct one. Of these cells the most suitable for laboratory use is the continuous acting hydrogen cell, which has been applied to conductivity measurements in the following way: The apparatus for the substitution method is arranged as in Fig. 1. The alter-

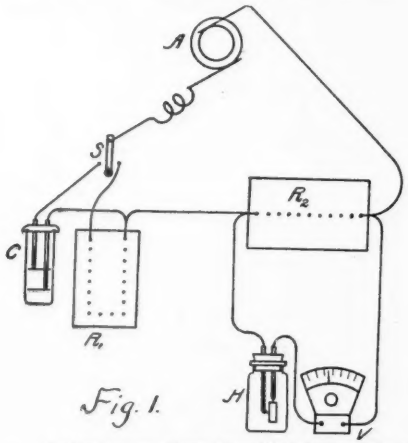


Fig. 1.

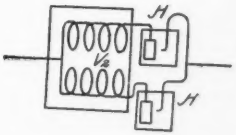


Fig. 2.

A is the source of the alternating current, S a switch allowing either C or R_1 to be in the circuit, C is the unknown resistance, R_1 and R_2 resistance boxes, H the hydrogen cell rectifier, and V the voltmeter or galvanometer.

nating current from A passes through the electrolyte in C and the non-inductive resistance R_2, to the terminals of which is connected a direct current instrument in series with the rectifying

[1] This Journal, **20**, 206 (1898).

[2] W. L. Hildburgh: This Journal. Also Ph.D. thesis in press and *School of Mines Quarterly*, July and October, 1900. Also *Elec. World and Eng.*, 1900.

cell. The reading of the instrument is noted when the current passes through the unknown resistance C, then S is moved so as to replace C by R_1, a non-inductive adjustable resistance, and this varied until the same reading is observed as before. If the proper precautions have been observed, the resistance of R_1 is equal to C and the conductivity may be calculated.

For the source of the alternating current we have found a small alternator to be more satisfactory than the small induction coils commonly used; there is, however, apparently no reason why a properly arranged coil should not be available. With the ordinary (Kohlrausch) electrodes and an alternating pressure of 2 volts the results were found to agree very satisfactorily with those obtained by the Kohlrausch-Ostwald method.

For the highest sensitiveness the following conditions should obtain. The resistance of R_2 which must be small compared with C, should be as large as possible.

The instrument V (galvanometer) should give large readings with small currents, and its resistance should be low. The frequency of the alternating current should be as low as allowable, the voltage as high as allowable, and the electrodes in C large. The area of the inert electrode in the rectifier should be small so as to give a high asymmetrical efficiency (percentage of rectification).

A considerably more sensitive arrangement is obtained by replacing R_2, H and V by a differential wound instrument whose two windings are exactly alike and are in series each with a rectifier. If these two coils are properly arranged all waves of one sign will go through one winding, and all of those of the opposite sign through the other (Fig. 2). This utilizes the whole of both half waves of current, instead of only a part of one, so that the deflection of the needle is very much greater.

The hydrogen cell rectifier can be "balanced" by adding a small electromotive force in series, so that up to a certain point a direct current instrument in series with it will give readings almost exactly proportional to the alternating current. Knowing the alternating voltage, the rectification constant of the hydrogen cell and the resistances of C and H, the resistance of C can be calculated directly from the readings of V. This method can be used without "balancing" the cell by calibrating V, using

different known resistances in place of C. The resistance of C can then be read directly from the scale of the instrument. In both these modifications the frequency of the alternating current must remain the same, and neither is as accurate as the first one by substitution.

The hydrogen cell rectifier permits the use of an optical detector instead of the telephone in the Kohlrausch-Ostwald method. The telephone is replaced by a resistance and a sensitive galvanometer in series with the "balanced" cell, arranged like R_2V and H in Fig. 2. The point on the slide wire which gives no deflection is then the same one as found by the telephone.

To "balance" the cell the circuit of a Leclanché is closed through a high resistance and a slide wire. The alternating current being stopped, an electromotive force is taken from the slide wire and sent through the rectifier, the slide being left just below the point which shows deflection. If "overbalanced" the cell will give a constant deflection, but if "underbalanced" the low voltage current obtained will give no deflection. An arrangement like Fig. 2 will give here greater sensitiveness, but the method of substitution as first described is the simplest and gives the best results.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, UNIVERSITY OF MICHIGAN.]

ON THE PREPARATION OF POTASSIUM XANTHATE FOR NICKEL DETERMINATIONS.

BY E. D. CAMPBELL.

Received April 23, 1900.

IN 1895 the author with W. H. Andrews published a method for the determination of nickel in nickel steel.[1] This method has been in use in this laboratory since its publication and has given very satisfactory results, provided the potassium xanthate used had been properly prepared. The potassium xanthate usually found on the market has not been satisfactory owing to the fact that the salt after making has not been carefully washed and dried. The practice in this laboratory has been to have each student prepare the potassium xanthate used in his own work.

[1] This Journal, 17, 125.

The method of preparation is as follows: A weighed amount of fused potassium hydroxide is placed with absolute alcohol in a tightly stoppered flask and digested cold, with occasional shaking, until solution is complete, except for the small amount of potassium carbonate usually present; 2.5 cc. of absolute alcohol should be used for each gram of potassium hydroxide.

The clear solution of potassium hydroxide is poured off from any undissolved carbonate into a beaker and cooled by standing in ice-water. Pure carbon disulphide is now gradually added with constant stirring until 1 cc. has been added for each gram of potassium hydroxide used. When all the carbon disulphide has been added the stirring is continued, the beaker being kept in ice-water until the temperature is reduced to 10° C. or below.

The formation of potassium xanthate takes place according to the reaction:

$$KOH + C_2H_5OH + CS_2 = KC_2H_5COS_2 + H_2O.$$

The precipitated salt is transferred best to a Buchner funnel in which a filter-paper has been laid, and the solution drawn out by means of a pump. When the solution has been drawn through, the precipitate is pressed rather firmly down in the funnel and washed once by pouring over it just enough absolute alcohol to cover it well. When the alcohol has been drawn through, the precipitate is washed twice in a similar manner with ether. The washed xanthate thus prepared is thoroughly dried at about 100° C. and after pulverizing is ready for use.

We have found that potassium xanthate made by the above method is perfectly stable, just as accurate results having been obtained with xanthate that had been kept three years as with the fresh material. With ordinary care in preparation, the yield of potassium xanthate is about 10 per cent. greater than the amount of potassium hydroxide used.

ANN ARBOR, MICH.,
April 16, 1900.